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Singlet Fission Rate: Optimized Packing of a Molecular Pair. Ethylene as a Model

Alexandr Zaykov,^{†,§} Petr Felkel,[‡] Eric A. Buchanan,^{||} Milena Jovanovic,^{||} Remco W. A. Havenith,^{⊥, #, ∇} R. K. Kathir,[⊥] Ria Broer,[⊥] Zdeněk Havlas,[†] and Josef Michl^{*, †, ||}

[†]Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, 16610 Prague 6, Czech Republic

[‡]Faculty of Electrical Engineering, Czech Technical University in Prague, 16627 Prague 6, Czech Republic

[§]Department of Physical Chemistry, University of Chemistry and Technology, 16628 Prague 6, Czech Republic

^{||}Department of Chemistry, University of Colorado, Boulder, Colorado 80309-0215, United States

[⊥]Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

[#]Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

[∇]Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 (S3), B-9000 Gent, Belgium

S Supporting Information

ABSTRACT: A procedure is described for unbiased identification of all π -electron chromophore pair geometry choices that locally maximize the rate of conversion of a singlet exciton into a singlet biexciton (triplet pair), using a simplified version of the diabatic frontier orbital model of singlet fission (SF). The resulting approximate optimal geometries provide insight and are expected to represent useful starting points for searches by more advanced methods. The general procedure is illustrated on a pair of ethylenes as the simplest model of a π -electron system, but it is applicable to pairs of much larger molecules, with dozens of non-hydrogen atoms, and not necessarily planar. We first examine the value of $|T^A|^2$, the square of the electronic matrix element for SF with initial excitation fully localized on partner A, on a grid of several billion geometries within the six-dimensional space of physically realizable possibilities. Several of the optimized pair geometries are somewhat unexpected, but all are found to follow the qualitative guidance proposed earlier. In the neighborhood of each local maximum of $|T^A|^2$, consideration of mixing with charge-transfer configurations and of excitonic interaction between partners A and B determines the SF energy balance and yields squared matrix elements $|T^*|^2$ and $|T^{**}|^2$ for the lower and upper excitonic states S^* and S^{**} , respectively. Assuming Boltzmann populations of these states, the geometry is further optimized to maximize k , the sum of the SF rates obtained from Marcus theory, and this reorders the suitable geometries substantially. At 87 pair geometries, the $|T^*|^2$ and $|T^{**}|^2$ values are compared with those obtained from high-level ab initio nonorthogonal configuration interaction calculations and found to follow the same trend. Finally, the biexciton binding energy at the optimized geometries is calculated. Altogether, 13 significant local maxima of SF rate for a pair of ethylenes are identified in the physically relevant part of space that avoids molecular interpenetration in the hard-sphere approximation. The three best geometries are twist-stacked, slip-stacked, and L-shaped. The maxima occur at the (five-dimensional) surfaces of seven six-dimensional “parent” regions of space centered at physically inaccessible geometries at which the calculated SF rate is very large but the two ethylenes interpenetrate. The results are displayed in interactive graphics. The computer code (“Simple”) written for these calculations is flexible in that it permits a choice of performing the search for local maxima in six dimensions on $|T^A|^2$, $|T^*|^2$, or k . It is available as freeware at <https://cloud.uochb.cas.cz/simple>.

INTRODUCTION

In the simplest description, singlet fission (SF) is a process in which a singlet exciton in an organic molecular solid shares its energy with a neighbor molecule in the ground state and joins it to form a singlet biexciton best described as two triplet excitons bound to each other, which then separate into two independent triplet excitons.^{1–9} The two triplets are at first coupled into a singlet biexciton, making the process spin-allowed and potentially very fast. The dissociation of the biexciton can be complicated as the system winds its way

through the up to nine nearly isoenergetic substates that result from the weak interaction of two triplets.

SF has been receiving considerable attention lately as an interesting intellectual challenge and because its exciton-multiplying nature provides an opportunity to circumvent the Shockley–Queisser theoretical limit¹⁰ on single-junction solar cell efficiency. A combination of a fully efficient SF material absorbing higher-energy photons with an ordinary material

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absorbing photons of lower energies could in principle avoid any current matching requirements and still increase the theoretical efficiency limit from about 1/3 to nearly 1/2.¹¹

The paucity of sturdy materials capable of performing SF with anywhere near unit efficiency is a major obstacle that stands in the way of its practical implementation. Given the number of additional conditions that any solar cell material must meet in order to permit efficient harvesting of excitons in the form of separated charges, it would be very useful to have general structural guidelines for the design of materials that provide a 200% triplet quantum yield. This requires a maximization of the rate of SF and simultaneous suppression of all competing processes. Harmful intramolecular processes such as intersystem crossing to a triplet state and internal conversion to the ground state of the same or an isomeric molecule are relatively easy to avoid by prior investigation of molecular photophysics in solution. It is harder to avoid in advance detrimental intermolecular processes such as decay of the initial singlet exciton to the ground state via excimers, charge-transfer species, and transient or stable bimolecular photoproducts, and decay of the first formed biexciton to the ground state via its various spin states, since they do not reveal their existence until the solid is investigated. In the present paper, we only deal with the optimization of the rate of one step of SF, the conversion of a singlet exciton into a singlet biexciton.

Fluorescence rate constants will usually be in the range of ns^{-1} , implying that the SF rate constants need to be close to the range of ps^{-1} to compete well. If the triplets are to be used for the production of charges, they need to separate readily and to be mobile and long-lived. In particular, they should not recombine rapidly to yield a single molecular excited state (which could be an excited- or ground-state singlet, first or higher triplet, or quintet). A long triplet lifetime carries its own dangers, especially the sensitization of residual oxygen to the highly reactive singlet state that tends to damage organic materials.

In order to be fast, singlet fission needs to be approximately isoergic or slightly exoergic,^{1,12–14} and this requires the energies of the excited states to be such that $E(S_1) \geq 2E(T_1)$ after all intermolecular interactions have been taken into account. Triplet–triplet annihilation to yield $S_1 + S_0$, $T_2 + S_0$, or $Q_1 + S_0$ will be endoergic when $E(S_1)$, $E(T_2)$, and $E(Q_1)$ all exceed $2E(T_1)$.

The maximization of the rate of SF in a material involves making two choices: (i) selecting the chromophore and (ii) optimizing its packing. The latter affects both the rate of formation of a singlet biexciton and the competition between its separation into two independent triplet excitons and its decay to one triplet exciton plus one ground-state molecule or to two ground-state molecules.

(i) Guidelines for the choice of chromophores that meet the energy criterion were derived from simple theoretical considerations a dozen years ago, and two partially overlapping classes of suitable structures were identified:¹⁵ large alternant hydrocarbons and biradicaloids. A derivative of a large alternant hydrocarbon, terrylene, has indeed been recently shown to perform well.¹⁶ Theoretical requirements for the use of biradicaloids have been elaborated further,^{17–20} and several biradicaloid structures have been identified as suitable candidates computationally.^{15,20–23} So far, only one of these proposals has been tested. This is 1,3-diphenylisobenzofuran, which was found to be highly efficient.²⁴ However, the triplet

yield was up to 200% in only one of its two very similar known crystal modifications and was a mere $\sim 10\%$ in the other.²⁵

(ii) The dramatic difference in the triplet yield in the two only slightly different crystal forms of this compound, and many other similar observations,^{25–36} illustrate the crucial importance of molecular packing for efficient singlet fission. Although preliminary attempts to develop crystal packing guidelines for efficient SF in a molecular pair have been published,^{1,5,37} no generally acknowledged recipes for packing that optimizes SF rates appear to be available. They would be useful for the synthesis of covalent dimers and possibly also for crystal engineering, as discussed below. Solids composed of optimized dimers remain largely unexplored, primarily because it has not been clear how to optimize the relative positions of the two monomers in the pair. Many covalent dimers have been investigated,^{38–48} but in the absence of general rules for optimal packing, their structures were usually selected for synthetic convenience rather than for optimization of SF.

Rules for the optimization of a mutual disposition of a pair of molecules to reach fast SF might be useful even for general molecular solids, but this is not guaranteed. There is now strong experimental evidence³⁵ that it is not always sufficient to consider only pairwise interactions between the nearest neighbors in a crystal, an approximation that is customary although not universal.^{49–55} Nevertheless, it is likely that rules for molecular pairs would have considerable merit not only for the synthesis of covalent dimers but also by providing hints concerning desirable molecular orientations in larger aggregates.

Most published quantum chemical calculations aimed at obtaining information on the variation of the SF matrix element with the geometry of a molecular pair covered only a small range of structures close to those observed in crystals or covalent dimers.^{56–65} The approach described presently is different in that we still only deal with molecular pairs but attempt to identify all particularly favorable pair geometries in the full six-dimensional space of possible physically accessible choices in an unbiased manner that avoids preconceived notions about the likely favorites.

We adopt the frontier orbital approximation and additional simplifications,⁶⁶ with details provided elsewhere.^{5,67} Presently, we use ethylene as the simplest π -chromophore model system, but the computational procedure is fast enough that it readily permitted an application to a pair of cibalackrot molecules, containing 36 non-hydrogen atoms each.⁶⁸ We also consider the implications of the results for the development of general back-of-the-envelope packing guidelines for singlet fission.^{1,2,5,34,37}

More serious testing of the value of the simple model developed here will be possible after it is applied to realistic chromophores. The results will hopefully provide guidance for efforts to prepare new SF solids by synthesis of covalent dimers and some hints for the general engineering of crystals. They may also provide suggestions for the interpretation of SF results for amorphous solids and of the effect of defects and grain boundaries in imperfect crystals. We recognize the limitations imposed by work with molecular pairs and the desirability of performing a complete unbiased search of orientations of molecular triples in 12 dimensions, or of even higher aggregates in even more dimensions.

The paper is organized as follows. First, we list the simplifying assumptions made.

Second, we describe briefly several levels of a simplified frontier orbital model of singlet fission at which the presently developed software permits a rapid complete search of the six-dimensional space for local maxima of a function relevant for SF, with due consideration of the limitations imposed by molecular impenetrability. The choice of functions is $|T^A|^2$, the squared electronic matrix element for initial excitation fully localized at A, $|T^*|^2$, the squared element for initial excitation delocalized between A and B with mixing with charge-transfer states included, and k , the sum of SF rates from the two exciton states with Boltzmann populations, obtained with Marcus theory. In any event, the geometry at the local maxima is subsequently reoptimized to maximize k . At the optimized geometries, the effect of intermolecular interactions on the biexciton dissociation energy is evaluated.

Third, the $|T^*|^2$ and $|T^{**}|^2$ values and the Davydov splittings $E(\text{DS})$ obtained at 87 favorable geometries by the approximate method are compared with those obtained from an ab initio calculation by the non-orthogonal configuration interaction method.⁶⁹

Fourth, we show how the 34 geometries favorable for $|T^A|^2$ within the accessible space relate to the only 13 parent geometries at which the true local maxima of $|T^A|^2$ are located, which are physically unrealizable because they involve molecular interpenetration. We also show how the 13 geometries optimized for k are derived from only seven extremely favorable but physically unrealizable parent geometries. In both cases, we provide an interactive three-dimensional perspective display of the favorable geometries and of the paths between the parents and the daughters.

METHOD

Assumptions. We can afford to introduce considerable simplifications, because we do not attempt to calculate absolute rates of SF, but only to identify approximate optimal geometries based on order-of-magnitude relative rates of conversion of a singlet exciton to a singlet biexciton calculated for a pair of molecules at different mutual dispositions. (i) Entropic effects are expected to be similar at different pair geometries, and free energy is approximated by potential energy. (ii) Interaction with the phonon bath is assumed to rapidly suppress initial coherent excitation of a superposition of the locally excited singlet and $^1\text{TT}^*$ biexciton states and to achieve vibrational equilibration. Marcus theory is used to obtain rate constants. Complete vibrational equilibration cannot be reached in the very fastest SF processes, but those are usually exothermic (cf. pentacene) and almost any molecular pair geometry will then be adequate, obviating the need for a search for optimal geometries. Presently, all other effects of intramolecular and intermolecular vibrations are ignored and the solid is assumed to be static. (iii) Only two molecules at a time are considered. The effect of delocalization of the initial singlet excitation over more than two chromophores is ignored, as is SF involving more chromophores than just a pair of neighbors. Approximate additivity is assumed if more than one distinct important neighbor is present. Possible coherent interactions between a chromophore and more than one of its neighbors, as well as interactions between two molecules that are mediated by other molecules, are ignored. This could be very inaccurate; cf. the different optical absorption spectra and singlet fission rates in the two crystal forms of 1,3-diphenylisobenzofuran, which differ significantly only in next-nearest-neighbor but not in

nearest-neighbor interactions (their calculated $|T^*|^2$ values are therefore nearly identical).^{25,35} (iv) Only the first step of SF is considered, in which the lower and upper exciton states, S^* and S^{**} , respectively, are converted into the singlet biexciton state, $^1\text{TT}^*$, and the subsequent competition between return to S^* or S^{**} , separation into free triplet excitons $T_1 + T_1$, and decay to the ground state, both of which may well occur via the $^5\text{T}_1\text{T}_1^*$ ^{70,71} and $^3\text{T}_1\text{T}_1^*$ states,⁷² is not. However, biexciton binding energies are calculated.

States of a Molecular Pair. We symbolize the two locally excited electron configurations that dominate the S^* and S^{**} states by S_1S_0 (A excited, B in the ground state) and S_0S_1 (B excited, A in the ground state) and the configuration that dominates the singlet biexciton $^1\text{TT}^*$ state by $^1\text{T}_1\text{T}_1$ (A and B both in the triplet state). We assume that the charge-transfer configurations $^1\text{D}^+\text{D}^-$ (A positive and B negative) and $^1\text{D}^-\text{D}^+$ (A negative and B positive) lie higher in energy and contribute to the description of the S^* , S^{**} , and $^1\text{TT}^*$ states but do not dominate. The asterisk sign at a wave function is used to indicate that mixing with the charge-transfer states has been included. For instance, the wave function $S_1S_0^*$ is a mixture of configurations S_1S_0 , $^1\text{D}^+\text{D}^-$, and $^1\text{D}^-\text{D}^+$.

We use the Fermi golden rule in the diabatic basis for the rate W of SF from an initial singlet state S

$$W = 2\pi\hbar^{-1} |\langle S | H_{\text{int}} | ^1\text{TT}^* \rangle|^2 \rho(E) \quad (1)$$

where H_{int} is the interaction Hamiltonian for A and B (the part of the electrostatic Hamiltonian that is absent if A and B are infinitely far apart) and $\rho(E)$ is the density of states at the energy of the $^1\text{TT}^*$ state. For initial singlet excitation localized at A and containing an admixture of the charge-transfer states, we substitute $S = S_1S_0^*$ and define $|T^A|^2 = |\langle S_1S_0^* | H_{\text{int}} | ^1\text{TT}^* \rangle|^2$. Similarly, for B, we substitute $S_0S_1^*$ and define $|T^B|^2 = |\langle S_0S_1^* | H_{\text{int}} | ^1\text{TT}^* \rangle|^2$. For initial excitation delocalized over both A and B, we substitute $S = S^*$ or $S = S^{**}$ and use $|T^*|^2 = |\langle S^* | H_{\text{int}} | ^1\text{TT}^* \rangle|^2$ and $|T^{**}|^2 = |\langle S^{**} | H_{\text{int}} | ^1\text{TT}^* \rangle|^2$.

Frontier Orbital Model. The matrix elements of H_{int} are evaluated approximately, using the frontier orbital model for the description of the initial and final wave functions. This model appears to be the simplest possible one that can still contain all of the essential physics. It has been in use for decades^{12,13,73,74} and has been summarized in recent reviews.^{1,2,5} Briefly, it places two electrons from each chromophore into the active space and allows them to occupy the highest occupied MO (HOMO, h) or the lowest unoccupied MO (LUMO, l) on either partner. All remaining electrons represent a fixed core. We simplify it further in that, in the resulting four-electron four-orbital active space, we only consider 5 of the 20 possible singlet configurations, similarly as was done in earlier work:⁷⁵ local single excitation on either partner, S_1S_0 and S_0S_1 , simultaneous local triplet excitation on both partners, $^1\text{T}_1\text{T}_1$, all three at the same energy, and the two charge-transfer configurations $^1\text{D}^+\text{D}^-$ and $^1\text{D}^-\text{D}^+$, both higher in energy by ΔE .

Simplification.^{2,5,66,67} The exact results⁶⁶ of the truncated frontier orbital model are too complicated for attempts to deduce simple qualitative guidance for locating the maxima of $|T^A|^2$ as a function of the mutual disposition of A and B and even for attempts to compute T^A for the billions of pair geometries that are required for an exhaustive mapping of the six-dimensional space defined by the mutual disposition of two molecules in contact. A series of approximations^{5,66,67} reduces

expressions for matrix elements of H_{int} greatly and makes the mapping easy.

The approximations are as follows: (i) In the evaluation of matrix elements of H_{int} , intermolecular overlap integrals are neglected; (ii) zero differential overlap⁷⁶ is adopted, (iii) frontier MOs are described in an orthonormal valence basis set of natural atomic orbitals⁷⁷ (NAOs); (iv) it is assumed that ΔE is the same for all pair geometries as long as the two partners touch; (v) the matrix elements $F_{\mu\nu}$ of the ground-state Fock operator between NAO μ on partner A and NAO ν on partner B are treated as Hückel resonance (hopping) integrals $\beta_{\mu\nu}$ and the approximations^{78,79} familiar from extended Hückel theory (EHT) are used to relate them to overlap integrals, $\beta_{\mu\nu} = k[(\alpha_\mu + \alpha_\nu)/2]S_{\mu\nu}$. In standard EHT, k is normally set equal to 1.75, and this works well for distances that are in the range of bond lengths. For distances on the order of the sum of van der Waals radii, which are relevant presently, the factor k needs to be reduced significantly. Using the Linderberg formula,⁸⁰ for $(2p-2p)_\pi$ and $(2p-2p)_\sigma$ interactions it is close to 1.0 for distances of 3–5 Å (Figure S1). We use 1.03.⁵

Diabatic States. We have used three procedures, I, II, and III, to define the initial and final diabatic states and to obtain their wave functions and the matrix elements of H_{int} between them. In the first two procedures, the initial excitation is assumed to reside on molecule A and the singlet exciton is $S_1S_0^*$ (represented by configuration S_1S_0 with an admixture of configurations $^1D^+D^-$ and $^1D^-D^+$). The mixing of the three configurations is dictated by H_{int} and is evaluated by first-order perturbation theory (procedure I) or by a 3×3 diagonalization (procedure II). In procedure III, the initial singlet excitation is delocalized over both molecules A and B. There are two independent initial diabatic states S^* and S^{**} that serve in parallel, and their populations are assumed to be in thermal equilibrium (Boltzmann distribution). Both are obtained from a 4×4 diagonalization of H_{int} in the basis of configurations S_1S_0 , S_0S_1 , $^1D^+D^-$, and $^1D^-D^+$.

The final diabatic state $^1TT^*$ is described by the configuration 1T_1T_1 with an admixture of configurations $^1D^+D^-$ and $^1D^-D^+$, as dictated by H_{int} . In procedure I, it is obtained by first-order perturbation theory, and in procedures II and III, by a 3×3 diagonalization. Before matrix elements between the initial and final states are evaluated, their wave functions are Löwdin orthogonalized.

Procedure I. The rationale for using this very approximate procedure at all is that, after a neglect of products of small numbers, it leads to a simple algebraic expression^{2,13} for T^A

$$T^A = T_{S_1S_0/T_1T_1} - (T_{S_1S_0/D^+D^-} - T_{D^+D^-/T_1T_1} + T_{S_1S_0/D^-D^+} - T_{D^-D^+/T_1T_1})/\Delta E \quad (2)$$

where $T_{X/Y} = \langle X|H_{\text{int}}|Y \rangle$. The first term on the right-hand side of this expression is usually referred to as “direct” and the second term as “mediated”. The T^A values calculated from eq 2 without any further approximations, such as neglect of intermolecular overlap, will be referred to as “exact” within the first-order perturbation theory version of the truncated frontier orbital model. They can be evaluated directly in the non-orthogonal basis using the formulas given in the appendix to ref 5 or after first performing a Löwdin orthogonalization and then using Slater rules. We find the latter more convenient computationally, but the former provides better qualitative insight.⁵

With the drastic approximations introduced above, this expression for T^A now takes the form (3) and fits on a single line instead of several pages. It only requires the knowledge of the expansion coefficients of the HOMO ($c_{\mu h}$, $c_{\nu h}$) and the LUMO ($c_{\mu l}$, $c_{\nu l}$) on A and B in terms of a valence basis set of natural atomic orbitals (NAOs), μ , κ on the first and ν , λ on the second partner, plus the intermolecular overlap integrals $S_{\mu\nu}$ and $S_{\kappa\lambda}$ between these NAOs:

$$T^A = 1.06\alpha_C^2[(3/2)^{1/2}/\Delta E][(\sum_{\mu\nu} c_{\mu h} c_{\nu h} S_{\mu\nu})(\sum_{\kappa\lambda} c_{\kappa l} c_{\lambda l} S_{\kappa\lambda}) - (\sum_{\mu\nu} c_{\mu h} c_{\nu l} S_{\mu\nu})(\sum_{\kappa\lambda} c_{\kappa l} c_{\lambda h} S_{\kappa\lambda})] \quad (3)$$

Here, the factor 1.06 originates in the conversion of overlap into resonance integrals (see below) and α_C is the extended Hückel theory Coulomb integral (electron binding energy) for the $2p_z$ orbital on carbon, -11.4 eV. As written, the equation applies to hydrocarbons. In the presence of heteroatoms, instead of using a uniform multiplication factor α_C , each overlap integral $S_{\alpha\beta}$ needs to be multiplied by $(\alpha_\alpha + \alpha_\beta)/2$, where α_α and α_β are the Hückel Coulomb integrals of the valence p_z orbitals of atoms of the appropriate elements.

Formula (3) is meant to be approximately valid at geometries where $|T^A|^2$ is large, permitting a search for local maxima. It is irrelevant for our purposes whether it also happens to be valid at geometries where $|T^A|^2$ is small. Its simplicity permits a formulation of very simple rules^{37,66} for maximization of T^A .

Procedure II. When ΔE is small, the perturbation theory formula (2) is expected to exaggerate the contribution of the mediated term to T^A . The purpose of procedure II is to provide a numerical check of the validity of first-order perturbation theory.

Procedure III. This procedure represents a step in the direction of a better description of physical reality at the expense of greatly reduced transparency. To obtain (i) the energies of both exciton states, the lower S^* and the upper S^{**} , and thus the Davydov splitting $\Delta E_{\text{DS}} = E(S^{**}) - E(S^*)$ and (ii) the contribution of intermolecular interactions to the energy balance, $\Delta E_{\text{SF}}(S^*) = E(^1TT^*) - E(S^*)$ and $\Delta E_{\text{SF}}(S^{**}) = E(^1TT^*) - E(S^{**})$, in the conversions of S^* and S^{**} to $^1TT^*$, we use the same approximations as in the evaluation of the matrix elements T and adopt the simplified formulas of refs 5 and 67, which take into account factors that affect the energies of the initial state with excitation on partner A, of the biexciton state, and of the final state with two separated triplets on the two partners. They are the direct interaction between transition densities on A and B and the contribution mediated by virtual charge-transfer states.^{81,82} The two-electron integral $4(h_{A1}l_{A1}h_{B1}l_{B1})$ that appears in the former was evaluated in the point-charge approximation.

Local Maxima of $|T^A|^2$ for a Pair of Ethylene Molecules. For the case of two rigid ethylene molecules, we decided to start with the simplest initial search of the six-dimensional space of partner disposition and look for the local maxima of $|T^A|^2$. The formula (3) simplifies to

$$|T^A|^2 = 1.15\alpha_C^4[3/2\Delta E^2](S_{2A1B}S_{2A2B} - S_{1A1B}S_{1A2B})^2 \quad (4)$$

where the NAOs on one ethylene are labeled 1A and 2A and those on the other are labeled 1B and 2B. To locate the maxima of the function $|T^A|^2 = f(X, Y, Z, R_x, R_y, R_z)$, where the variables describe the mutual disposition of ethylenes A and B, we start with the two molecules superimposed and oriented

with their long molecular axis x along the laboratory axis X , the short in-plane molecular axis y along Y , and the out-of-plane molecular axis z along Z . We rotate one of the molecules successively by angles R_x , R_y , and R_z around the three molecular axes and then translate it along the laboratory axes by distances X , Y , and Z (see section 8 in the Supporting Information). Note that $1.15\alpha_C^4[3/2\Delta E^2]$ is a multiplicative constant that scales the values of T^A but can be ignored in the search for local maxima.

For the evaluation of the overlap integrals, we represented the carbon $2p_z$ NAOs in terms of a contracted Gaussian basis set without diffuse functions, taken from Pople's 6-311G basis set.⁸³ The diffuse functions were removed because they artificially add small local maxima to the outer reaches of the NAOs (Figure S3). The expansion coefficients of NAOs in terms of contracted Gaussians were obtained utilizing Weinhold's NBO analysis^{84,85} and the SCF wave function of ethylene. Finally, the HOMO and LUMO were constructed as in-phase and out-of-phase combinations of Löwdin orthonormalized $2p_z$ NAO on each carbon atom, respectively. The geometry of the ethylene molecule was optimized at the B3LYP/6-311+G* level. For the evaluation of T^A , we used $\Delta E = 1$ eV. The evaluation of the right-hand side of formula (4) at a single geometry takes only a few tens of μ s of CPU time, making it possible to map out rapidly and completely the part of the six-dimensional space of pair geometries in which the two chromophores are close to each other. The evaluation was performed on a grid in which X was varied from -7 to $+7$ Å, Y was varied from -6.75 to $+6.75$ Å, and Z was varied from -6.5 to 6.5 Å by increments of 0.25 Å, and R_x , R_y , and R_z were varied from 0 to 350° by increments of 10° , for a total of $57 \times 55 \times 53 \times 36^3 \approx 8 \times 10^9$ geometries.

Exclusion of Inaccessible Space. Before identifying all significant local maxima of $|T^A|^2$ and of k , geometries in which the chromophores interpenetrate are removed. The procedure is described in the Supporting Information. When searching for relations between daughter and parent extrema, the repulsion energy is gradually reduced using a reduction parameter (Figure S2).

Identification of Local Maxima. The first step in the search for the local maxima of $|T^A|^2$, which will also automatically find all optimal geometries for $|T^B|^2$, was an identification of regions of likely local maxima of f by finding geometries at which $f_{n-1} < f_n > f_{n+1}$ for three sequential grid points centered at n in all six dimensions. After removing duplicates, about 13 000 such preliminary maxima were located. When neither $|T^A|^2$ nor $|T^B|^2$ is large, their linear combinations $|T^{**}|^2$ and $|T^{*}|^2$ cannot be large, either. Next, starting from each preliminary maximum, the real maxima of $|T^A|^2$ were located by optimization. The process started with a line search in direction $-\mathcal{H}^{-1}\mathbf{g}$ ($\mathcal{H}$ is the Hessian matrix, and $\mathbf{g}$ is the gradient) followed by Davidon–Fletcher–Powell (DFP)⁸⁶ optimization steps, repeated until the gradient norm drops below 10^{-8} eV²/Å or eV²/deg and geometry changes by less than 10^{-6} Å or deg. The initial direction in each DFP step followed the $-\mathcal{H}^{-1}\mathbf{g}$ vector. The first and second derivatives needed for optimization were calculated numerically, with the first derivatives using a five-point formula and the second derivatives using a three-point formula.

Marcus Theory for SF Rates. The effect of intermolecular interaction on reaction energy balance, due to exciton (Davydov) splitting, needs to be evaluated at the pair geometry

of each local maximum of $|T^A|^2$ before the geometry can be truly recommended as suitable for singlet fission. The SF rate could be estimated in various ways, from inspection to a serious calculation, using, for instance, Redfield theory, and we believe that a very approximate theory is appropriate for our purpose, estimation of relative rates at the various minima. In the simplest version of Marcus theory, the effects of $\rho(E)$ are reflected in two parameters, the reorganization energy λ and the reaction energy balance. We assume that SF is isoergic before the intermolecular interaction is taken into account and thereafter is endoergic by $E(^1\text{TT}^*) - E(\text{S}^*)$. We neglect the external reorganization energy and assume the internal reorganization energy to be dictated by the chromophore itself and to be independent of the pair geometry. Reorganization energy λ was obtained as $\{E[\text{T}_1, q(\text{S}_1)] + E[\text{T}_1, q(\text{S}_0)] - 2 \times E[\text{T}_1, q(\text{T}_1)]\}$,⁸⁷ where $q(\text{X})$ is the monomer equilibrium geometry in state X . Marcus rate constants^{88–90} were calculated using eqs 5 and 6. Rates contributed by the two singlet excimer states S^* and S^{**} were added assuming two-level Boltzmann equilibrium populations,⁹¹ eq 7.

The search for local maxima of k started at each of the 34 local maxima of $|T^A|^2$ obtained by procedure I and varied the geometry of the molecular pair to maximize the value of k obtained from eqs 5–7, using $\Delta E_{\text{SF}}(\text{S}^*)$, $\Delta E_{\text{SF}}(\text{S}^{**})$, $|T^*|^2$, and $|T^{**}|^2$ obtained by procedure III.

$$k(\text{S}^*) = (2\pi/\hbar)|T^*|^2(4\pi\lambda k_{\text{B}}T)^{-1/2} \exp[-(\Delta E_{\text{SF}}(\text{S}^*) + \lambda)^2/4\pi\lambda k_{\text{B}}T] \quad (5)$$

$$k(\text{S}^{**}) = (2\pi/\hbar)|T^{**}|^2(4\pi\lambda k_{\text{B}}T)^{-1/2} \exp[-(\Delta E_{\text{SF}}(\text{S}^{**}) + \lambda)^2/4\pi\lambda k_{\text{B}}T] \quad (6)$$

$$k(\text{SF}) = \{1 - [\exp(-\Delta E_{\text{DS}}/k_{\text{B}}T) + 1]^{-1}\}k(\text{S}^*) + \{[\exp(-\Delta E_{\text{DS}}/k_{\text{B}}T) + 1]^{-1}\}k(\text{S}^{**}) \quad (7)$$

Biexciton Binding Energies. For compatibility with the other approximations, the contribution of intermolecular interactions to the binding energy of the biexciton $\Delta E_{\text{BB}} = 2E(\text{T}_1) - E(^1\text{TT}^*)$ was assumed to result only from differential stabilization by interaction with the charge-transfer configurations $^1\text{D}^+\text{D}^-$ and $^1\text{D}^-\text{D}^+$. Using the approximations described above, this leads to eq 8.⁶⁷

$$\begin{aligned} \Delta E_{\text{BB}} &= 1.06(3/2)(|\langle l_{\text{A}} | \hat{F} | l_{\text{B}} \rangle|^2 + |\langle h_{\text{A}} | \hat{F} | h_{\text{B}} \rangle|^2)/\Delta E \\ &= 1.06(3/2)(|\sum_{\mu\nu} c_{\mu\text{A}} c_{\nu\text{B}} S_{\mu\nu}|^2 + |\sum_{\mu\nu} c_{h\mu} c_{h\nu} S_{\mu\nu}|^2)/\Delta E \end{aligned} \quad (8)$$

Non-Orthogonal Configuration Interaction (NOCI). At many of the geometries of local maxima obtained by the simple calculations, $|T^A|^2$ and ΔE_{DS} were also evaluated by the far more accurate ab initio NOCI method.^{69,92} First, for each partner A and B, the following calculations were performed: (i) CASSCF(2,2) for the ground state, (ii) ROHF calculation for the S_1 (HOMO to LUMO excitation) state, (iii) ROHF calculation for the T_1 state, (iv) ROHF calculation for the D^+ state (radical cation), and (v) ROHF calculation for the D^- state (radical anion) (6-311G basis set, with GAMESS-UK⁹³).

Subsequently, many-electron basis functions (MEBFs, $\Phi_{\text{AB}}(IJ) = A[\Psi_{\text{A}}(I)\Psi_{\text{B}}(J)]$) were constructed by forming antisymmetrized product wave functions from the monomer wave functions $\Psi_{\text{A}}(I)$, describing state I of partner A, and

$\Psi_B(J)$, describing state J of partner B. The following six singlet MEBFs were produced: $\Phi_{AB}(S_0S_0)$, $\Phi_{AB}(S_1S_0)$, $\Phi_{AB}(S_0S_1)$, $\Phi_{AB}(^1T_1T_1)$, $\Phi_{AB}(^1D^+D^-)$, and $\Phi_{AB}(^1D^-D^+)$. Both Hamiltonian and overlap matrix elements between the MEBFs were calculated using the GronOR⁹⁴ code, which is based on GNOME.⁹⁵

The effective electronic coupling between diabatic states i and j was evaluated according to $t_{ij}^{\text{eff}} = H_{ij} - S_{ij}(H_{ii} + H_{jj})/2(1 - S_{ij}^2)$. To allow for delocalization, a NOCI calculation was performed to form the diabatic states $c_1D_{AB}(S_1S_0) + c_2D_{AB}(S_0S_1)$. Similarly, the effect of the charge-transfer (CT) configurations was taken into account by performing two NOCI calculations, one in the basis of the MEBFs describing S_1S_0 and/or S_0S_1 , $^1D^+D^-$ and $^1D^-D^+$, and one in the basis of the MEBFs describing 1T_1T_1 , $^1D^+D^-$, and $^1D^-D^+$. Subsequently, the Hamiltonian and overlap matrices were transformed to the basis of the diabatic states, allowing the evaluation of electronic coupling. Weights of the MEBFs in the final states were assigned according to the Gallup and Norbeck scheme.⁹⁶

RESULTS

The Parent and Daughter Local Maxima of $|T^A|^2$ and k . The calculated reorganization energy was 1.4 eV under the assumption that the ethylene molecule remains planar, which was made in deference to the anticipated use of the procedure for larger conjugated π -electron systems.

After removing duplicates, about 13 000 preliminary local minima of the negative of the search function ($-f$) for $|T^A|^2$ were found with procedure I. They correspond to maxima of the function $|T^A|^2$ that are located in the physically accessible part of the six-dimensional space of all pair geometries. Upon further optimization, many converged to identical geometries, and in the end, only 34 independent local maxima of $|T^A|^2$ resulted (Supporting Information). The pair geometries at these local maxima are shown on the left in Figure 1, and the important properties of the top 12 are collected in Table 1. Starting at the 34 maxima of $|T^A|^2$, a similar process using procedure III led to 13 local maxima of k (Figure 2 and Table 2). The tables permit a comparison of the results of procedures I–III.

The accessible local maxima of $|T^A|^2$ are mostly located at the five-dimensional surfaces of inaccessible segments of the six-dimensional search space that are centered at the true local maxima of the function $|T^A|^2$ itself. At these geometries, this function acquires values that often are orders of magnitude larger than those in the physically accessible parts of the total six-dimensional space. In order to gain a better understanding of the nature of the function $|T^A|^2$, it is interesting to correlate the physically accessible and meaningful local maxima that we found (“daughter maxima”) with their inaccessible “parent” local maxima. The correlation was obtained by starting at each of the daughter maxima and allowing the pair geometry to follow the direction of steepest descent of the negative of the search function f defined in eq 5 while gradually reducing the magnitude of hard-sphere repulsion in small steps (Supporting Information).

In Table 1, the results for the first 12 accessible daughter maxima of $|T^A|^2$ found with procedure III are compared with those for $|T^A|^2$ and $|T^B|^2$ obtained with procedures I and II (results for all of these maxima are shown in Table S1). These 12 geometries can be seen in Figure 1 and in more detail in Figure 3. All results obtained with procedure III for both the

Figure 1. Black numbered daughter and red numbered parent structures of a pair of ethylenes ordered vertically by the decadic logarithm of $|T^A|^2$ and mutually color correlated.

accessible daughter and inaccessible parent maxima, as well as the paths connecting them, are displayed in the interactive Figure 4 (if reading the printed version, go to https://dcgi.fel.cvut.cz/home/felkepet/Molecule/index-Figure4_T34.html).

Table 2 collects the results for all 13 geometries that maximize k obtained with procedure III. They are also found in Figure 2 and in more detail in Figure 5. All results obtained at the 13 geometries that maximize k obtained with procedure III for both the daughter and parent maxima, as well as the paths connecting them, are displayed in the interactive Figure 6 (if reading the printed version, go to https://dcgi.fel.cvut.cz/home/felkepet/Molecule/index-Figure6_k13.html).

In the interactive Figures 4 and 6, the geometries at the local maxima are shown in three-dimensional views with projections onto three walls of an octant. One ethylene molecule (orange carbon atoms) is located at the origin. A viewer-selected second ethylene molecule appears in its appropriate position in a 3D view, located in the central 3D display area. The reader is able to select visualized geometry, set visualization options, and change the viewpoint arbitrarily.

See <https://dcgi.fel.cvut.cz/home/felkepet/Molecule/>.

The maxima are sharp, and the $|T^A|^2$ values fall off rapidly as the geometry begins to deviate from optimal. The slopes are anisotropic. In the steepest direction, $|T^A|^2$ and k usually fall off to half their value upon translation by 0.1 Å or rotation by 5°, whereas, along the gentlest slope, the typical values are 0.5 Å and 30° (Table S2).

Results for $|T^*|^2$, $|T^{}|^2$, and ΔE_{D5} from NOCI Calculations.** The results of ab initio non-orthogonal configuration interaction calculations are included in Table S1. It lists results obtained for the coupling elements and Davydov splitting at 37 geometries at which $|T^A|^2$ obtained with procedure I in the 6-311G basis and 37 additional ones

Table 1. Energies in meV from Procedures I, II, and III (6-311G Basis Set) for the First 12 Physically Accessible Ethylene Pair Structures at Local Maxima of $|T^A|^2$ ^a

No.	$T^{A2} + T^{B2}$		$T^{*2} + T^{**2}$	$ T^A $		$ T^B $		$ T^* $	$ T^{**} $	$4(h_{AA}I_A/h_{BB}I_B)$	ΔE_{DS}	$\Delta E_{SF}(S^*)$	$\Delta E_{SF}(S^{**})$	ΔE_{BB}
	I	II	III	I	II	I	II	III	III	III	III	III	III	III
1	2.6×10^5	1.0×10^5	8.7×10^4	430	270	270	270	280	78	-415	580	466	-114	194
2	1.7×10^5	6.8×10^4	6.8×10^4	410	260	0.0	0.0	180	180	0	0	92	92	229
3	2.0×10^4	1.3×10^4	1.3×10^4	140	110	0.0	0.0	81	81	0	0	-72	-72	159
4	2.2×10^3	1.9×10^3	1.9×10^3	47	43	0.0	0.0	31	31	0	0	3	3	42
5	9.0×10^2	7.9×10^2	7.5×10^2	29	28	5.9	5.9	21	17	348	381	161	-220	53
6	5.1×10^2	3.8×10^2	2.9×10^2	18	16	13	13	17	3.4	-66	233	58	-175	142
7	1.9×10^3	1.9×10^3	1.1×10^3	17	15	40	40	30	15	-246	399	134	-265	143
8	3.1×10^2	2.5×10^2	1.9×10^2	15	13	9.3	9.3	13	4.2	432	544	225	-319	103
9	2.1×10^2	2.0×10^2	2.0×10^2	14	14	0.0	0.0	9.9	9.9	0	0	-17	-17	25
10	2.6×10^2	2.2×10^2	2.6×10^2	10	9.5	12	12	11	16	247	334	139	-196	75
11	6.6×10^1	6.2×10^1	6.2×10^1	8.2	7.9	0	0	5.6	5.6	0	0	-29	-29	31
12	1.1×10^2	1.0×10^2	9.7×10^1	5.0	4.8	9.3	9.3	9.4	3.0	155	119	55	-63	26

^aSee text; $\Delta E_{DS} = E(S^{**}) - E(S^*) =$ Davydov splitting; $\Delta E_{SF}(S^*) = E(^1TT^*) - E(S^*)$ and $\Delta E_{SF}(S^{**}) = E(^1TT^*) - E(S^{**})$ are the energy balance of SF from S^* and S^{**} , respectively (positive energy balance = endoergic SF); $\Delta E_{BB} =$ biexciton binding energy.

Figure 2. Black numbered daughter and red numbered parent structures of a pair of ethylenes ordered vertically by the decadic logarithm of k and mutually color correlated.

obtained in the 6-311+G basis had a local maximum, plus 13 at which k had a local maximum in the 6-311G basis. A comparison with the results obtained with procedure III is shown in Figure 7.

DISCUSSION

The purpose of developing the method described in this Article is an investigation of the feasibility and utility of complete and unbiased searches of the six-dimensional space of geometries of molecular pairs in search of those that are particularly suitable for SF. We have shown that the search is feasible; presently for the model case of a pair of ethylenes but

elsewhere^{5,67,68,97} also for pairs of much larger molecules. The discussion of the results will be divided into three parts. They deal with general aspects, with the results for the SF matrix element, and with the results for relative SF rates, respectively. We remind the reader that the squared matrix elements $|T^A|^2$ and $|T^B|^2$ are merely auxiliary quantities, except that their functional form is useful for the derivation of simple rules. The primary results of our search are the optimal geometries, and the secondary results are the squared matrix elements $|T^*|^2$, the relative rate constants k/k_0 , the Davydov splitting ΔE_{DS} , and the biexciton binding energy ΔE_{BB} . The calculated local maxima of k as a function of pair geometry are relatively sharp, and it will be challenging to reach such geometries by crystal engineering or covalent dimer synthesis. Fortunately, thermal vibrations are likely to broaden the maxima considerably.

The general questions that need to be addressed are the following:

(i) How useful are the pair geometries identified by our procedure likely to be? Since we merely attempted to optimize the rate at which SF occurs and did not try to avoid geometries at which competing decay processes are also rapid, only a subset of the pair geometries found can be expected to afford high triplet yields by SF. It is however quite likely that pair geometries that are not among those selected presently for fast SF will not be competitive. If no other decay processes take over, fluorescence will. The utility of the procedure thus consists of a vast reduction of the number of possibilities facing a theoretician wishing to apply a more accurate method of calculation to find optimal geometries for SF or facing a synthetic chemist desirous of packing his chromophores optimally for SF, whether by crystal engineering or by preparation of covalent dimers or oligomers.

(ii) Are the pair geometries identified as optimal sufficiently accurate? The agreement of the trends produced by the present rapid procedure III with those yielded by the much more elaborate ab initio NOCI method suggests that the accuracy is adequate for a rough identification of desirable pair geometries, even though it may not predict relative rates reliably. Figure 7A shows that the accuracy is excellent at those geometries at which T^2 is the largest, as expected from the design of the approximate method. Already at geometries at which T^2 is two orders of magnitude below its maximum, the scatter of points in the log-log plot in Figure 7 is high, and at

Table 2. SF Rate Constants in s^{-1} and Energies in meV from Procedure III (6-311G Basis Set) for the 13 Physically Accessible Ethylene Pair Structures at Local Maxima of k_{SF}^a

No.	$ T^* $	$ T^{**} $	$T^{*2} + T^{**2}$	$4(h_A l_A h_B l_B)$	ΔE_{DS}	$\Delta E_{\text{SF}}(S^*)$	$\Delta E_{\text{SF}}(S^{**})$	ΔE_{BB}	k_{SF}/k_0^b
1	1.2×10^2	1.2×10^2	3.0×10^4	0	0	-75	-75	222	1
2	1.2×10^2	7.8×10^1	2.0×10^4	-188	26	-65	-91	231	7.1×10^{-1}
3	6.8×10^1	6.8×10^1	9.3×10^3	0	0	-61	-61	135	2.4×10^{-1}
4	2.3×10^1	2.3×10^1	1.0×10^3	0	0	2	2	31	7.8×10^{-3}
5	2.3×10^1	2.3×10^1	1.0×10^3	0	0	2	2	31	7.8×10^{-3}
6	7.2	7.2	1.0×10^3	0	0	-21	-21	25	1.2×10^{-3}
7	4.0	4.0	3.2×10^1	0	0	-28	-28	29	4.5×10^{-4}
8	1.3×10^1	1.3×10^1	3.4×10^2	290	298	132	-166	29	1.9×10^{-4}
9	1.3×10^1	1.3×10^1	3.4×10^2	291	298	132	-166	29	1.9×10^{-4}
10	2.4	2.4	1.2×10^1	0	0	-1	-1	4	9.5×10^{-5}
11	6.8×10^{-1}	6.8×10^{-1}	9.3×10^{-1}	0	0	-1	-1	2	7.6×10^{-6}
12	7.1×10^{-1}	0.0	5.0×10^{-1}	238	238	119	-119	1	7.1×10^{-7}
13	1.6×10^{-1}	1.6×10^{-1}	4.8×10^{-2}	0	0	0	0	0	3.8×10^{-7}

^aSee text; $\Delta E_{\text{DS}} = E(S^{**}) - E(S^*) = \text{Davydov splitting}$; $\Delta E_{\text{SF}}(S^*) = E(^1\text{TT}^*) - E(S^*)$ and $\Delta E_{\text{SF}}(S^{**}) = E(^1\text{TT}^*) - E(S^{**})$ are the energy balance of SF from S^* and S^{**} , respectively; $\Delta E_{\text{BB}} = \text{biexciton binding energy}$. ^b $k_0 = 1.1 \times 10^9 \text{ s}^{-1}$.

Figure 3. (A) Physically realizable geometries of pairs of ethylene molecules at the first six largest local maxima of $|T^A|^2$ ($2p_z$ atomic orbitals shown schematically). Calculated values of $\log_{10}|T^A|^2$ (red), the Davydov splitting (blue), and the biexciton binding energy (gold); energy in meV. (B) Physically realizable geometries of pairs of ethylene molecules at the next six largest local maxima of $|T^A|^2$ ($2p_z$ atomic orbitals shown schematically). Calculated values of $\log_{10}|T^A|^2$ (red), the Davydov splitting (blue), and the biexciton binding energy (gold); energy in meV.

even smaller values of T^2 , it gets much worse still. However, this is of no consequence for our purposes.

(iii) Is it reasonable to adopt the ZDO approximation, in which the direct term in the first-order perturbation expression (2) vanishes? The results then reflect only that part of the matrix element that is mediated by the charge-transfer configurations. Our initial evaluations of expression (2) for a pair of ethylenes without ZDO suggested that the direct

contribution is indeed negligible, at least at geometries near the local maxima of $|T^A|^2$. The same conclusion was reached by authors who performed calculations for pairs of other chromophores, such as tetracene⁹² and pentacene.¹³ A previous suggestion to the contrary, based on a qualitative estimate for a pair of tetracene chromophores,⁹⁸ seems to have been mistaken. The situation could easily be different at geometries for which $|T^A|^2$ is small,³¹ but these are of no

Figure 4. Interactive: Click on https://dcgi.fel.cvut.cz/home/felkepet/Molecule/index-Figure4_T34.html. Steps leading from ethylene pair geometries of physically realizable local daughter maxima to physically unrealizable local parent maxima of the function $|T^A|^2$ as intermolecular repulsion is gradually removed (see text; $|T^A|^2$ was obtained from procedure I and the rest from procedure III). Click here for instructions on how to manipulate the interactive figure: <https://dcgi.fel.cvut.cz/home/felkepet/Molecule/fig-instructions.html>.

interest for our search. It might perhaps also be different in conjugated dimers (intramolecular SF), which lie beyond the scope of this paper.

(iv) Could the accuracy of the simple method be easily improved? The assumption that ΔE , the energy difference between the locally excited and the charge-transfer configurations, is the same for all pair geometries as long as the two partners touch, is not really necessary. It could be replaced by an evaluation of ΔE at each geometry, where the effective dielectric constant of the medium would be one of the input parameters. We have performed a series of calculations to evaluate this possibility. In the end, we concluded that the variation in ΔE with pair geometry is small enough that the likely error in the calculated ΔE values would not be significantly smaller than the error introduced by assuming that it is constant. We also examined the effect of the choice of an arbitrary constant value for ΔE , such as 1 or 2 eV, on the geometries evaluated as optimal, and we found that it is small. Perhaps in the future a more elaborate calculation of ΔE can be introduced, but at the moment, we prefer to keep the method as simple as possible.

One could also remove the assumption that SF would be isoergic if intermolecular interactions did not affect the state energies. Given that these energies, especially those of triplets, are rarely known to an accuracy better than 0.1 eV from experiment or from calculations and that state energies in molecular solids, particularly those of charge-transfer states, suffer from even more uncertainty, we again decided in favor of keeping the model and the algebra as simple as possible. Since endoergicity significantly in excess of 0.3–0.4 eV generally prevents fast SF at room temperature, while significant exoergicity most likely makes SF fast at nearly all pair geometries but incurs unacceptable energy losses by converting too much photon energy into heat, a focus on isoergic SF does not seem to represent a significant constraint for a theory that

aims at identification of optimal geometries and does not attempt to predict any absolute rate constants.

(v) Even if the present approach is accurate enough, how relevant is it for actual experiments? There is no doubt that the results are relevant for understanding SF in solution, in amorphous solids, and in those covalent dimers in which through-bond interactions between the partners have a negligible effect, such that they are not in direct conjugation. However, as noted above, for the most important case of solids with long-range order, the relevance of any method that only considers a pair of molecules at a time still remains to be proven.³⁵ We believe that the next step in this line of research needs to be the development of a similar unbiased full-space search procedure based on the consideration of at least three molecules at a time. The high dimensionality of the search will require a replacement of the present primitive brute-force grid search by a more sophisticated algorithm.

The following comments are appropriate regarding the molecular pair geometries that optimize the square of the SF matrix element:

(vi) Table 1 shows that the results of the most primitive first-order perturbation theory (procedure I) are in qualitative agreement with those of procedure II, which uses a 3×3 diagonalization. The nature and order of the resulting optimized geometries are also similar to those of the even more elaborate procedure III with its 4×4 diagonalization. A detailed inspection of Figures 1–3 and 5 and especially of the paths that lead from daughter to parent geometries in Figures 4 and 6 reveals how remarkably closely the optimized geometries adhere to the simple rule⁶⁶ for maximizing $|T^A|^2$, deduced from the algebraic solution (2) offered by procedure I: At the best geometries, one of the AOs of ethylene A overlaps strongly with both AOs of ethylene B, while the other AO of ethylene A overlaps with the AOs of ethylene B as little as possible. This requirement has revealed some pair geometries of types that have not been considered in the past. The agreement with the

Figure 5. (A) Physically realizable geometries of a pair of ethylenes at the six best local maxima of k_{SF} ($2p_z$ atomic orbitals shown schematically). $\text{Log}_{10} k_{\text{SF}}$ relative to the best ($k_{\text{SF}} = 1.1 \text{ ns}^{-1}$) structure **1b** (red), the Davydov splitting (blue), and the biexciton binding energy (gold); energy in meV. (B) Physically realizable geometries of a pair of ethylenes at the next seven best local maxima of k_{SF} ($2p_z$ atomic orbitals shown schematically). $\text{Log}_{10} k_{\text{SF}}$ relative to the best ($k_{\text{SF}} = 1.1 \text{ ns}^{-1}$) structure **1b** shown in part A (red), the Davydov splitting (blue), and the biexciton binding energy (gold); energy in meV.

simple rule suggests that even the proposed generalization of this rule for larger π -electron systems³⁷ may be useful, as examined elsewhere.^{67,97}

(vii) When intermolecular repulsions are ignored and molecules are allowed to penetrate, orders of magnitude higher values of the SF matrix element $|T^A|^2$ and rate constants k are obtained (Figures 1 and 2). This suggests that under pressure faster SF could be achieved. This is undoubtedly true, but it is not at all clear whether higher triplet yields would result, since competing processes such as excimer formation, intermolecular charge-transfer state generation, and biexciton decay might be accelerated just as much or even more.

The best parent (unrealizable) molecular pair geometries at the maxima of the $|T^A|^2$ function obtained without any consideration of intermolecular repulsions involve a very severe interpenetration of the two ethylene molecules. Their transformation into the realizable daughter structures involves a large increase in the intermolecular distance. The five best parent structures in Figure 1 are (1) in-plane collinear, (2) in-plane T-shaped, (3) orthogonally tilted, (4) out-of-plane T-

shaped, and (5) twisted out-of-plane T-shaped. Apparently because of the very substantial increase in intermolecular separation upon going to daughter structures, these pair geometries produce daughter structures whose $|T^A|^2$ values are quite small. Only the sixth and higher parent structures, which involve less severe molecular interpenetration and less change upon going to a daughter structure, produce important daughters. The best three daughter structures are the (1) slip-stacked, (2) twist-stacked, and (3) L-shaped, each derived from a parent structure of a similar shape (Figure 1, Table 1). Among these, the general notion of slip-stacked structure has received the most attention in the past from numerous authors, starting with the realization that perfect stacking leads to a vanishing SF matrix element.¹ The forbiddenness is alleviated by a slip along the HOMO–LUMO transition moment direction, which removes a plane of symmetry perpendicular to this direction. As long as such a plane is present, the S_1S_0 (and T_1S_0) configurations will be antisymmetric and the S_0S_0 and T_1T_1 configurations will be symmetric with respect to it, and the purely electronic matrix element $\langle S_1S_0 | H_{\text{int}} | T_1T_1 \rangle$ must

Figure 6. Interactive: Click on https://dcgi.fel.cvut.cz/home/felkepet/Molecule/index-Figure6_k13.html. Steps leading from physically realizable local daughter maxima to physically unrealizable local parent maxima of k_{SF} as intermolecular repulsion is gradually removed (see text; $|T^A|^2$ was obtained from procedure I and the rest from procedure III). Click here for instructions on how to manipulate the interactive figure: <https://dcgi.fel.cvut.cz/home/felkepet/Molecule/fig-instructions.html>.

Figure 7. Plot of $\log_{10}(T^2)$ (A) and of Davydov splitting (B) obtained with procedure III and with ab initio non-orthogonal configuration interaction (NOCI). Correlation line (dotted red): $\log_{10}(T^2)^{\text{PROC. III}} = 0.76 \log_{10}(T^2)^{\text{NOCI}} + 1.44$, $T^2 = (T^*)^2 + (T^{**})^2$. Color coding of the largest values of T^2 provides a correlation of corresponding points in parts A and B.

vanish. A vibronic term may be present if the initial and final state differ by an odd number of quanta of antisymmetric vibration (cf. ref 31).

It is noteworthy that the 12th parent structure in Figure 1 and the nearly identical 7th parent structure in Figure 2 look very much like planar 1,3-butadiene, whose $2A_g$ state has 1TT character.

Although an understanding of the dependence of the SF matrix element on the geometry of a molecular pair is essential, the effect of intermolecular interactions on state energies and the resulting SF rate is just as important. This is clear from a

comparison of Tables 1 and 2 and of Figure 1 with Figure 2, Figure 3 with Figure 5, and Figure 4 with Figure 6. Therefore, we next discuss the results dealing with SF reaction rates. We need to reemphasize that the present discussion of the relative merits of various pair geometries considers only the rate of formation of the biexciton and its binding energy, and not the yield of free triplet excitons. In a complete treatment, one would also need to evaluate the decay rates of both the initial singlet exciton and the resulting biexciton.

(viii) The factor $\rho(E)$ in the Fermi golden rule applied to the rate of SF has been treated by many authors, for example,

via microscopic dynamics,^{12–14} using a simple kinetic model,⁹⁹ or in the Marcus theory formalism,⁵⁶ which we adopted presently. Marcus theory generally underestimates the SF rate by orders of magnitude, and its appeal is the minimal demand that it makes on detailed knowledge of the properties of the specific chromophore used. We believe that it is adequate for the present purpose, estimation of relative rates. Its assumption of thermal equilibration cannot possibly be justified in the cases of ultrafast SF, such as pentacene, but these are primarily the strongly exothermic ones, which do not need to be treated.

The results summarized in Figure 2 and Table 2 reveal a great similarity between the optimal pair geometries that maximize the SF matrix element and those that maximize the SF rate, and the geometries of the $|T^A|^2$ maxima 2, 3, 4, 9, and 11 in Table 1 are nearly identical with those of maxima 1, 3, 5, 6, and 7, respectively, in Table 2. Structures 5, 8, 9, 10, 11, and 12 in Table 1 closely resemble structures 8, 9, both 7 and 10, 2, 10, and both 4 and 5, respectively, in Table 2. What is very different are the functional values at the maxima. The three winners as best pair geometries for k_{SF} are all familiar as the three winners for $|T^A|^2$. Now, the twist-stacked (1) and the slip-stacked (2) geometries share the first place, and the L-shaped (3) geometry is almost as good. For all other geometries, k_{SF} is at least an order of magnitude smaller. These three would then be the geometries to recommend for further computation or synthesis if one were to use ethylene as the chromophore.

The factor that weeds out many of the geometries that appeared favorable when judged by $|T^A|^2$ is endoergicity caused by a large Davydov splitting ΔE_{DS} . At room temperature, almost all of the singlet exciton population then resides in the greatly stabilized lower exciton state S^* , from which SF is strongly endoergic. For the seven best geometries optimized for k listed in Table 2, the Davydov splitting ΔE_{DS} listed in Table 1 is very small or zero, and so is SF endoergicity. This is not so for the best geometry optimized for $|T^A|^2$ (Table 1), which has ΔE_{DS} of about 0.6 eV. It might be possible to compensate the deleterious effect of a large ΔE_{DS} by choosing a chromophore in which the triplet excitation energy is sufficiently below half the singlet excitation energy and excitation into the lower exciton S^* is allowed.

We note in passing that the magnitude of ΔE_{DS} is likely to play a role not only in the estimation of the relative value of the SF rate k , which is the subject of the present paper, but also in the estimation of the rates of competing processes, which are beyond its framework. Specifically, attempts to predict the rates of the formation of excimers in molecular solids will need to consider the ease of molecular displacement within the solid after initial excitation (low-frequency acoustic phonons) and the driving force for such displacement. If ΔE_{DS} is large already at the equilibrium geometry of the ground state, it is likely to increase further upon molecular displacement toward an excimer geometry, providing a driving force for such displacement. Thus, from purely qualitative considerations, a large ΔE_{DS} is likely to indicate a predisposition toward excimer formation in competition with SF.

Inspection of Table 1 shows that the magnitude of ΔE_{DS} is primarily dictated by the size of the excitonic interaction term $4(h_{\text{A}}|h_{\text{B}})$. This is the electrostatic interaction energy of the transition densities of the S_0 to S_1 promotion on partners A and B and can be easily visualized from the knowledge of the shape of the HOMO and the LUMO. This then allows the formulation of an augmented qualitative rule for judging the suitability of a pair geometry for SF.⁶⁷ It is possible to estimate

the magnitude of the excitonic interaction term even more simply by inspection of the transition dipole moments (dipoles of the transition densities), and it is then easily understood why geometries in which the two ethylene $\text{C}=\text{C}$ bonds are mutually perpendicular are favored for SF whereas those in which the two transition dipoles interact strongly produce low values of k and are eliminated from competition.

SUMMARY

We have described a computationally undemanding method for the approximate but unbiased determination of all optimal geometries of large nonpenetrating π -electron chromophore pairs that are particularly likely to undergo rapid SF and ranking them by the expected speed. The method has been applied to ethylene as the simplest model system and revealed some unanticipated favorable structures. It is also applicable to much larger π -electron systems, including those deviating from planarity. The software developed for the purpose is freely available at <https://cloud.uochb.cas.cz/simple>.

We suspect that the greatest deficiency of the procedure that requires future attention is not so much the limited accuracy of the geometries produced and of the relative rates predicted but two other problems: (i) Failure to evaluate the rates of competing processes such as excimer and charge-transfer state formation, which prevents the prediction of triplet yields. Although a general qualitative warning against a large Davydov splitting that likely provides a driving force for these undesirable events is useful, it is not sufficient. (ii) The consideration of only two molecules at a time and the resulting neglect of many-body interactions.

The removal of these shortcomings should be the next target of efforts. In the meantime, the method can be used for covalent dimers, amorphous solids, or solutions and further to obtain inspiration for the design of solids in which long-range order is present and of starting geometries for searches by more advanced methods.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b08173.

The distance dependence of the proportionality constant between overlap and resonance integrals, the hard-sphere repulsion potential and its use to convert daughter to parent maxima, the radial density function in the 6-311+G basis set, the ethylene pair geometries for Figure 7, $|T^A|^2$ and k_{SF} at their local maxima, and the ethylene pair geometries at the maxima (PDF)

AUTHOR INFORMATION

Corresponding Author

*josef.michl@colorado.edu

ORCID

Eric A. Buchanan: 0000-0002-3908-3275

Remco W. A. Havenith: 0000-0003-0038-6030

Ria Broer: 0000-0002-5437-9509

Josef Michl: 0000-0002-4707-8230

Notes

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