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**Alternative Mechanisms for Supercollision  
Induced Chemical Reactions**

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# Alternative Mechanisms for Supercollision Induced Chemical Reactions

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*Abstract:*

The observation of chemical transformations to infer the presence and propensity of large collisional energy transfer from hot, ground state, polyatomic donors (i.e. supercollisions) is re-evaluated. Consideration of electronic relaxation as well as photochemical processes leave open the possibility that such chemical changes could be a result of mechanisms not considered in the original work. In the case of azulene sensitized isomerization of quadricyclane, the role of naphthalene is suggested; for the effect of hexafluorobenzene on cyclobutene, a mechanism involving the transient intermediate difluorocarbene is delineated.

*Letter:*

The chemical sensitization of chemical reactions following collisional energy transfer with hot, ground state donors was the first reported observation of the phenomenon of chemical 'strong' collisions.<sup>1, 2</sup> The measured reactivity was rationalized by the process of multiple quanta of vibrational energy from a complex

polyatomic being transferred to an acceptor molecule in a single collision, providing over 10,000 cm<sup>-1</sup> of energy (about 1/3 of the total vibrational energy) needed to promote a chemical transformation. Interpretation of large rotational and translational excitation by Mullin et al.<sup>3</sup> as a consequence of ‘supercollisions’ has been recently questioned based upon experimentally characterized photodissociation processes.<sup>4</sup> Consideration of previously measured photorelaxation processes<sup>5</sup> and recently studied photoreactive processes<sup>6</sup> suggests alternative explanations for the isomerization of cyclobutene observed by Morgulis et al.<sup>2</sup> and the isomerization of quadricyclane measured by Hassoon et al.<sup>1</sup>

Morgulis et al.<sup>2</sup> have found that when hexafluorobenzene is photoexcited in the presence of cyclobutene, products such 1,3-butadiene and other C<sub>2</sub> species can be observed. The minimum amount of energy required for such chemical reactions begins at about 34 kcal, and this energy may be transferred from hexafluorobenzene to cyclobutene via many possible pathways. The possibility of triplet sensitized isomerization is dismissed based upon quantitative arguments which do not agree with published literature measurements. Using the estimated triplet quantum yield at 257 nm excitation of 0.10 from the work of Haller<sup>7</sup> and lifetime of 4 × 10<sup>-7</sup> s from the work of Phillips<sup>5</sup> the corrected estimate of triplet sensitization according to the equation of Morgulis et al.<sup>5</sup> is

$$\begin{aligned}\phi(^3\text{CB}) &= \phi(^3\text{HFB}) \cdot k_{\text{coll}} \cdot P_{\text{cb}} \cdot \tau_{\text{T}} \\ &= (0.10) \times (12.5 \times 10^6) \times (0.01) \times (4 \times 10^{-7}) = 5 \times 10^{-3}\end{aligned}$$

which can account for Morgulis' measurement of  $9 \times 10^{-4}$ . Of central importance is the triplet lifetime measurement: Morgulis et al. assume a 100 picosecond ( $10^{-10}$  s)  $T_1 \rightarrow S_0$  intersystem crossing lifetime which differs greatly from the Phillip's measured value. One may compare the benzene triplet quantum yield  $\phi(^3BZ) \sim 0.6$ <sup>8</sup> and  $T_1 \rightarrow S_0$  lifetime,  $1.3 \times 10^{-5}$  s.<sup>9</sup> The 'heavy-atom' or Z-effect on intersystem crossing is cited as the roughly two order of magnitude effect by Phillips.

The accuracy of the Cundall and biacetyl method for triplet determination in the case of hexafluorobenzene is a likely cause of much of the lifetime uncertainty. Since trans-2-butene requires about 60 kcal of triplet energy to isomerize<sup>10</sup> it will show a very small yield with a less energetic donor, in the same manner that Morgulis et al. observe little isomerization of cyclopropane, a process requiring 65 kcal.<sup>2</sup> The biacetyl method requires about 65 kcal to induce phosphorescence<sup>11</sup> and this emission can be quenched by hexafluorobenzene as observed by Phillips. Noting that the phosphorescence spectrum of hexafluorobenzene in EPA glass is extended from 350 to 600 nm with a maximum at 425 nm<sup>5</sup>, it is plausible that the hexafluorobenzene triplet origin is near 2.1 eV (48 kcal), with the triplet vibronic state or sublevel most strongly coupled radiatively to the ground state near 2.9 eV. Once hexafluorobenzene has crossed to the triplet manifold, either from biacetyl sensitization or intersystem crossing from  $S_1$ , rapid vibrational equilibration will relax the system to a state which can only promote reactions such as the 32.4 kcal needed to isomerize cyclobutene.<sup>12</sup>

Triplet sensitization cannot account for the appearance of  $C_2$  products that are reported to be about 20% as prevalent as the primary product. Morgulis et al. attribute these to photodecomposition of the butadiene, yet the nearest allowed transition starts at 220 nm,<sup>13</sup> past typical bandpass limits for filters whose transmission peaks at 255 nm. This is consistent with Morgulis' observation that cyclobutene, with its absorption beginning at 200 nm,<sup>14</sup> was not found to photofragment during a control experiment.<sup>2</sup>

To account for the entire distribution of products we propose a mechanism involving the photodecomposition products of hexafluorobenzene, which is known to degrade slightly following infra-red and UV excitation<sup>15</sup> as well as interact with numerous organic compounds during decomposition.<sup>16</sup> Moreover, evidence of  $CF_2$  production based upon fluorescence<sup>17</sup> and infra-red absorption<sup>18</sup> has been recently complemented with measurement of products such as  $C_2F_4 + C_4F_2$ ,  $C_3F_3$ ,  $C_5F_3 + CF_3$  and  $CF_2 + C_3F_4$ <sup>6</sup> using a molecular beam technique.<sup>19</sup> The most translationally energetic fragment observed was difluorocarbene,  $CF_2$ , whose time-of-flight spectrum and translational energy distribution are shown in figure 1. Because this distribution is peaked close to zero and has a slim tail extending to about 1 eV we would not expect it to cause significant rotational or translation excitation to a buffer gas in the manner that the fast HCN from pyrazine would.<sup>4</sup> However, several of hexafluorobenzene's decomposition products are likely to be reactive towards unsaturated centers. For example, difluorocarbene is an electrophile that can attack both the cyclobutene and butadiene products giving rise to fragment species.<sup>20</sup> Initial addition of the carbene across the olefinic bond will be extremely exothermic, providing the internal energy



required for subsequent rearrangements and fragmentations. A simple ab initio calculation (HF/6-31 optimized) predicts this step to be exothermic by 99 kcal ; thus, the strained three and four membered rings in the bicyclic intermediate should have sufficient energy for ring opening and rearrangement. Two mechanisms are detailed in figure 2 that are consistent with the less reactive behavior of cyclopropane ( in which all carbon centers are saturated) and the production of C<sub>2</sub> hydrocarbon species which would require an ‘ultra-collision’ (i.e. c. 100 kcal) if no photochemical mechanisms were present. A detailed analysis of the final product mixture for species such as 3,3-difluoro-1,4-pentadiene could provide valuable clues to the extent of reactions between the hydrocarbon and halogenated species.

The first reported ‘very strong collision’ involved the isomerization of quadricyclane sensitized by photoexcited azulene.<sup>1</sup> Central to the analysis was the production of ground state azulene from S<sub>2</sub> (2 <sup>1</sup>A<sub>1</sub>) to S<sub>0</sub> (1 <sup>1</sup>A<sub>1</sub>) in 3.2 ns.<sup>21</sup> Since this lifetime is measured from the total fluorescence decay rate (S<sub>0</sub> ← S<sub>2</sub> for azulene, not S<sub>0</sub> ← S<sub>1</sub>) contributions from S<sub>1</sub> ← S<sub>2</sub>, T<sub>n</sub> ← S<sub>2</sub> and T<sub>1</sub> ← S<sub>2</sub> processes are included. Work done by Knight et al.<sup>22</sup> shows similar lifetimes and a strong isotope effect that is attributed principally to the S<sub>1</sub> ← S<sub>2</sub> process.<sup>23</sup> The S<sub>1</sub> (1 <sup>1</sup>B<sub>1</sub>) ← S<sub>2</sub> (2 <sup>1</sup>A<sub>1</sub>) radiative transition has been observed<sup>24</sup> and will be in competition with radiationless internal conversion. Intersystem crossing into the triplet manifold from S<sub>2</sub> (ΔE(S<sub>2</sub>-S<sub>0</sub>)= 30 000 cm<sup>-1</sup>) or from S<sub>1</sub> (ΔE(S<sub>1</sub>-S<sub>0</sub>)= 16 000 cm<sup>-1</sup>, ΔE(S<sub>1</sub>-T<sub>1</sub>)= 2 000 cm<sup>-1</sup>)<sup>25</sup> is likely and the S<sub>0</sub> ← T<sub>1</sub> relaxation more rapid than benzene (for benzene, (ΔE(S<sub>1</sub>-S<sub>0</sub>)= 38 000 cm<sup>-1</sup>,

$\Delta E(S_1-T_1) = 8\,600\text{ cm}^{-1}$  ). Azulene will likely show a reduced triplet lifetime similar to hexafluorobenzene based upon its electronic structure, but can still provide a relatively 'long-lived' triplet state (whose quantum yield  $\times$  lifetime  $\sim 10^{-8}$  s) that can provide the 33.5 kcal needed to overcome the isomerization barrier of quadricyclane.<sup>26</sup>

An alternative explanation for the azulene system involves photoisomerization to the more thermodynamically stable naphthalene species. Such a rearrangement can be induced thermally<sup>27</sup> as well by ultraviolet light with a quantum efficiency of about  $5 \times 10^{-6}$  at 313 nm and 10 mtorr total pressure.<sup>28</sup> The experimental conditions of wavelength (330 nm maximum), pressure (c. 10 mtorr) and exposure time (c. 5 hours) reported by Hassoon et al. (ref. 1) are very similar to those of Comtet and Mettee (ref. 19). The difficulty of getting a naphthalene-free sample of azulene is evidenced by the purification and crystallization procedures reported by Olmsted<sup>29</sup>, whose efforts brought the measured naphthalene impurities to 0.065%. Even in relatively small quantities, naphthalene absorbs strongly ( ${}^1B_{3u} \leftarrow {}^1A_{1g}, \pi\pi^*$ ) at 315 nm<sup>30</sup> and it very efficiently induces the isomerization of quadricyclane<sup>31</sup> as shown in Figure 3. The mercury arc lamp should provide light in this range, for UV cut-off filters such as the Corning 7-60 will pass light down to 300 nm, shielding direct absorption by quadricyclane but not by naphthalene. The buffer gas pressure dependence of sensitization will follow the same pattern for isomerization as for a 'supercollision' mechanism. This last conjecture could be tested by putting naphthalene in the cell with quadricyclane and irradiating the mixture under conditions identical to the azulene experiment.

In summary, the relaxation processes associated with sensitizers that show supercollision behaviour should be considered carefully when photoexcitation processes are involved. The possibility of photodissociation products such as radicals which can initiate chemical transformations and long-lived electronic states that can transfer energy may be more effective mechanisms for inducing chemical reactions than collisions with vibrationally excited, ground state molecules.

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*Figure Captions:*

Figure 1.

The time-of-flight spectrum and translational energy distribution of difluorocarbene ( $\text{CF}_2$ ) following infra-red multiphoton pumping of hexafluorobenzene. The primary chemical process observed was  $\text{C}_6\text{F}_6 \rightarrow \text{CF}_2 + \text{C}_5\text{F}_4$ . Although difluorocarbene was the most translationally excited product measured, its corresponding kinetic energy distribution is not likely to cause large rotational or translational excitation (supercollision behaviour) following collisional energy transfer.

Figure 2.

The conversion of cyclobutene to 1,3-butadiene and other  $\text{C}_2$  species may be rationalized based upon the transient breakdown products of hexafluorobenzene. Addition of difluorocarbene leads to a highly energetic and strained bicyclic intermediate that can undergo further rearrangement and dissociation to a variety of products.

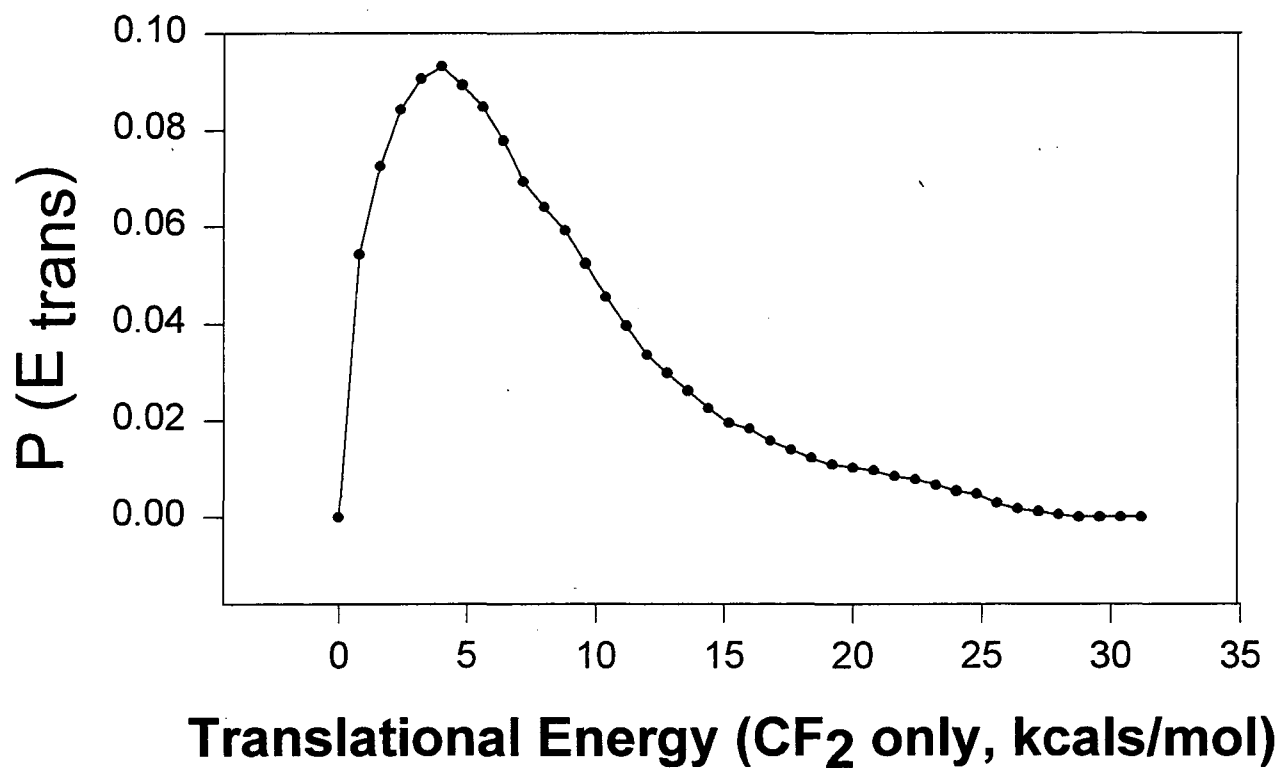
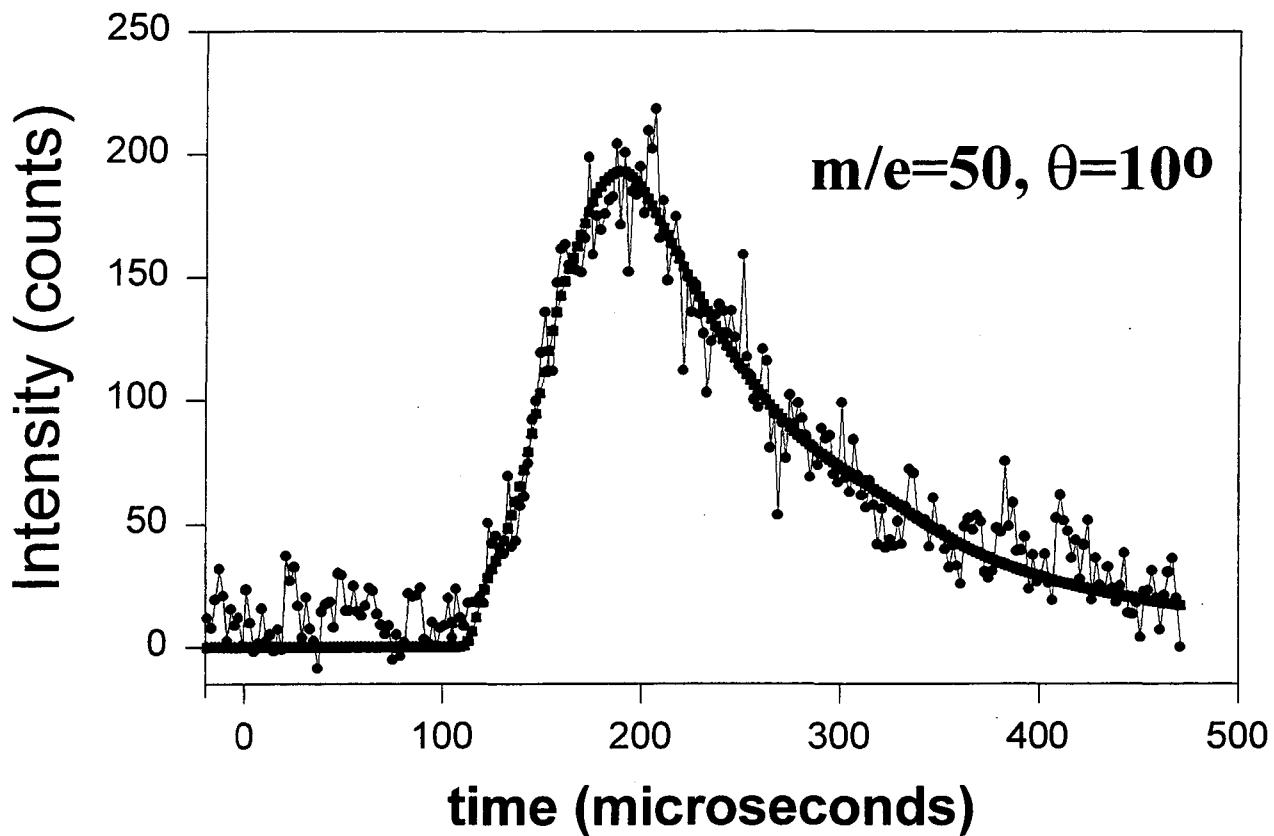
Figure 3.

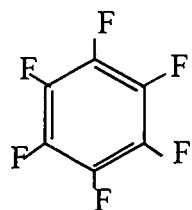
The conversion of quadricyclane to norbornadiene can be explained by photoconversion of azulene into naphthalene followed by triplet sensitized isomerization. The experimental conditions of running a mercury lamp discharge over several hours should allow for a small but significant amount of the more thermodynamically stable naphthalene to accumulate and drive the relatively efficient second step.

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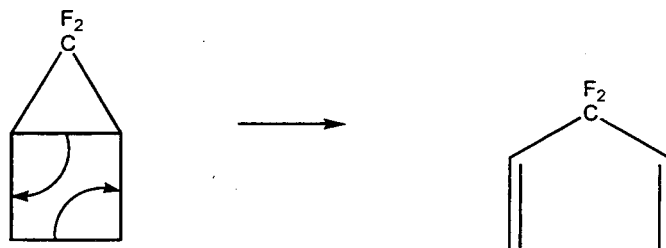
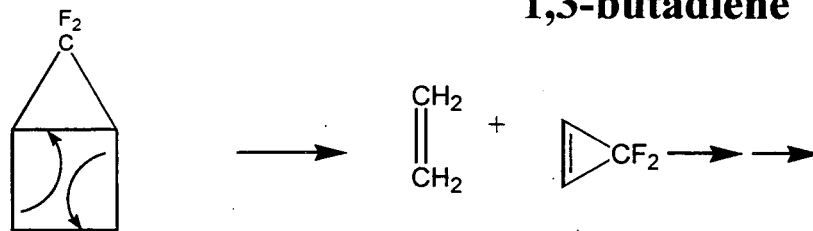
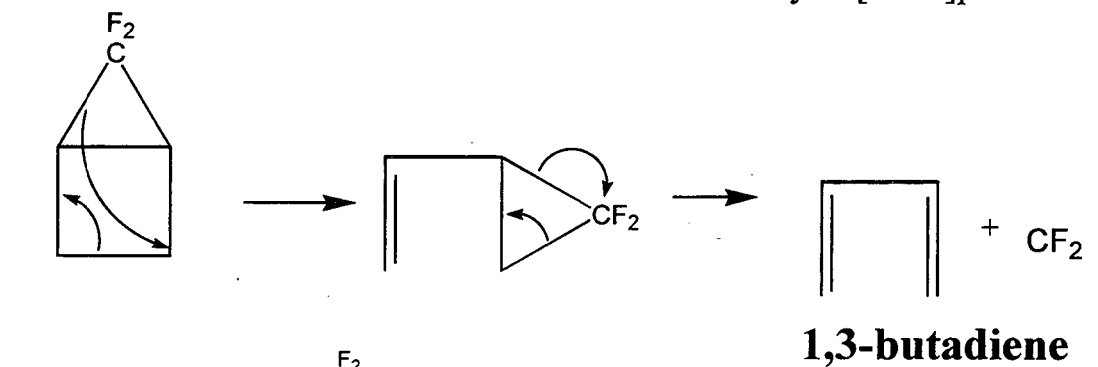
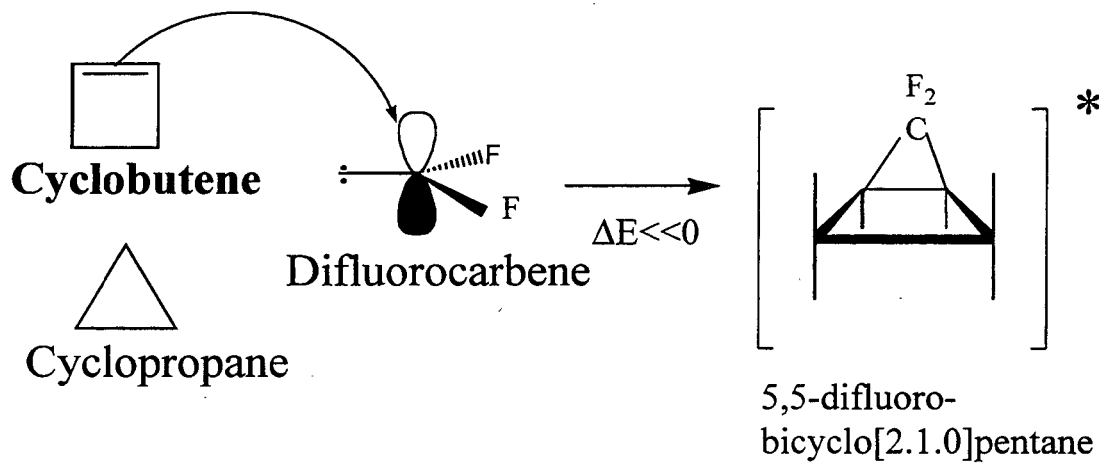
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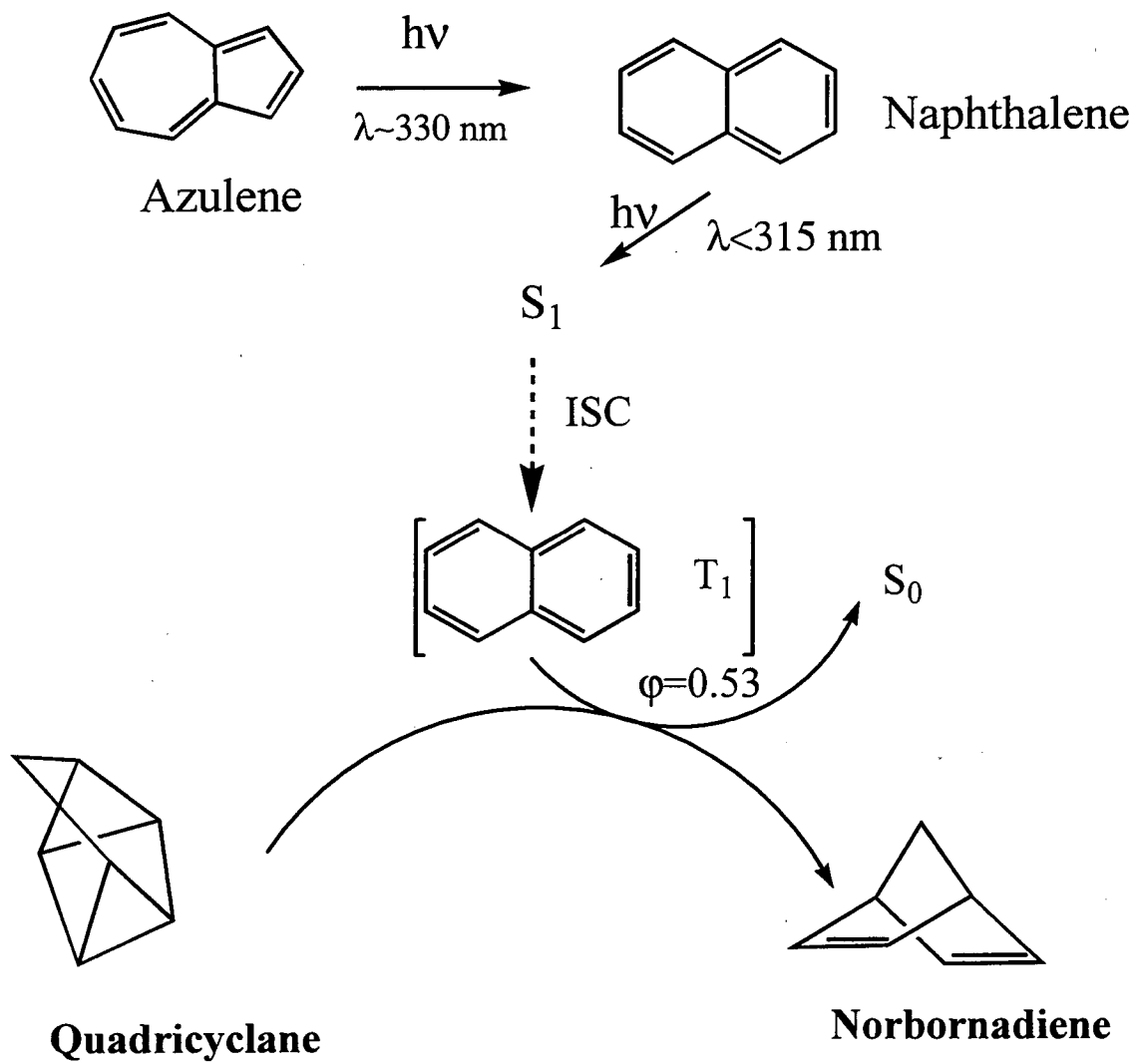




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