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# The Excited State Antiaromatic Benzene Ring: A Molecular Mr. Hyde?

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**Abstract:** The antiaromatic character of benzene in its first $\pi\pi^*$ excited triplet state ($T_1$) was deduced more than four decades ago by Baird through usage of perturbation molecular orbital (PMO) theory [*J. Am. Chem. Soc.* 1972, **94**, 4941], and since then it has been confirmed through a range of high-level quantum chemical calculations. With focus on benzene we now first review theoretical and computational studies that examine and confirm Baird's rule on reversal in the electron count for aromaticity and antiaromaticity of annulenes in their lowest triplet states as compared to Hückel's rule for the ground state ($S_0$). We also note that the rule according to quantum chemical calculations can be extended to the lowest singlet excited state ($S_1$) of benzene. Importantly, Baird, as well as Aihara [*Bull. Chem. Soc. Jpn.* 1978, **51**, 1788], early put forth that the destabilization and excited state antiaromaticity of the benzene ring should be reflected in its photochemical reactivity, yet, today these conclusions are often overlooked. Thus, in the second part of the article we review photochemical reactions of a series of benzene derivatives that to various extents should stem from the excited state antiaromatic character of the benzene ring. We argue that benzene can be viewed as a molecular "Dr. Jekyll and Mr. Hyde" with its largely unknown excited state antiaromaticity representing its "Mr. Hyde" character. The recognition of the "Jekyll and Hyde" split personality feature of the benzene ring can likely be useful in a range of different areas.

## 1. Introduction

Benzene is the single most important aromatic molecule. Yet, this is the situation in the electronic ground state ($S_0$). Theoretical and computational studies with a variety of different approaches and methods have shown that benzene is antiaromatic in its lowest $\pi\pi^*$ excited states of triplet and singlet multiplicities, *i.e.*, in its $1^3B_{1u}$ ($T_1$) and $1^1B_{2u}$ ($S_1$) states, respectively.[1-12] The theoretical foundation for the antiaromatic character of benzene in its $T_1$ state was provided by Colin Baird in 1972 when he analyzed both [4$n$]- and [4$n$+2]annulenes in their lowest $\pi\pi^*$ triplet states by usage of perturbation molecular orbital (PMO) theory,[1,13,14] and concluded that the rule for aromaticity and antiaromaticity in this state is opposite to what is the case for the closed-shell singlet state given by Hückel's rule. *I.e.*, [4$n$]annulenes are aromatic and [4$n$+2]annulenes are antiaromatic. He specifically wrote that the "prime example of triplet state antiaromaticity occurs in the diallylic form of benzene". Similar as aromaticity is reflected in the properties of compounds with presumed aromaticity, antiaromaticity is reflected in certain properties, *e.g.*, a high reactivity and propensity to distort from their most antiaromatic high-symmetry structure.[15-18] Indeed, with regard to reactivity Baird wrote that the "antiaromaticity associated with the triplet state of benzenoid hydrocarbons is predicted to yield drastic changes in the intermolecular reactivity compared to the ground state."

A few years after Baird's formulation, Aihara used Hückel molecular orbital (HMO) theory and employed a characteristic polynomial to describe the localized structure of a conjugated hydrocarbon which allowed him to analytically calculate the resonance energies of any kind of conjugated compounds.[2] He analyzed annulenes with Hückel and Möbius orbital topologies in

their ground states as well as in their first $\pi\pi^*$ states (multiplicity not considered) and concluded that "either conformation of any annulene in the excited state can be predicted to have an aromatic character opposite to that in the ground state". In particular, the resonance energies of benzene in the $S_0$ state and in the lowest $\pi\pi^*$ excited state are $0.273\beta$ and $-0.692\beta$, respectively. Based on this finding he wrote that "Hückel benzene (*i.e.*, ordinary benzene) is the most stable annulene in the ground state, but the resonance energy becomes greatly negative when it is electronically excited. Such a situation is best represented by a high reactivity of this compound in the excited state."

Experimentally, the area of excited state (anti)aromaticity (ES(A)A) was opened by Wan and Krogh in 1985 when exploring the photosolvolysis of 9-fluorenol in methanol.[19] They concluded that "the driving force for the photosolvolysis is believed to be the formation of an aromatic $4\pi$ cationic system in the excited state". The group of Wan in the 80s and 90s then pioneered experimental applications of excited state aromaticity (ESA) for photochemical formation of [4$n$]annulenic species.[20-37] Within theoretical and computational chemistry the field laid dormant from the early 80s until 1998 when two papers on the aromaticity of the first triplet states of [4$n$]annulenes reopened the field.[38,39] Schleyer and co-workers verified the aromaticity of [4$n$]annulenes in their lowest triplet states through high-level quantum chemical calculations of aromatic stabilization energies, nucleus independent chemical shifts (NICS) and magnetic susceptibilities,[38] and Zilberg and Haas formulated a valence bond theoretical description of the aromaticity of [4$n$]annulenes.[39] Subsequently, it has been shown computationally for cyclobutadiene, benzene and cyclooctatetraene that Baird's rule is also expandable to the $S_1$ state.[4,5,8,40]

[4$n$+2]Annulenes are often particularly stable in their $S_0$ states and, thus, their excited state properties are of wide importance. Yet, the early formulations of Baird and Aihara on the implications of the excited state antiaromaticity for the photochemistry of benzene and benzene derivatives are generally overlooked by the broad (photo)chemical community. We find that it is time that this is changed, particularly in light of the findings from recent computational investigations. Indeed, with this background we argue that one can consider benzene as a molecular version of Dr. Jekyll and Mr. Hyde, the split personality drama described in the 1886 novella by R. L. Stevenson.[41] We claim that benzene in its $S_0$ state takes the role of the respectable Dr. Jekyll while the evil Mr. Hyde corresponds to benzene in its $T_1$ and $S_1$ states. To support our claim we first describe previous theoretical and computational work which concern the antiaromaticity of benzene in its lowest electronically excited states. We then review the known photochemical reactions of benzene and a variety of different benzene derivatives, and we particularly view these reactions with the background knowledge on the excited state antiaromaticity (ESAA) of the benzene ring. Can the photoreactions be described as a way to alleviate the ESAA character of the benzene ring? We argue that the drive for ESAA alleviation is a factor that influences the photoreactivity of benzene derivatives (Figure 1). The drive of the benzene ring to reduce its excited state antiaromaticity through various photoreactions then corresponds to the evil actions of Mr. Hyde, and we argue that strong evidence for this characteristic is provided by the sheer number of different photoreactions in which a benzene ring is actively involved in the transformations.
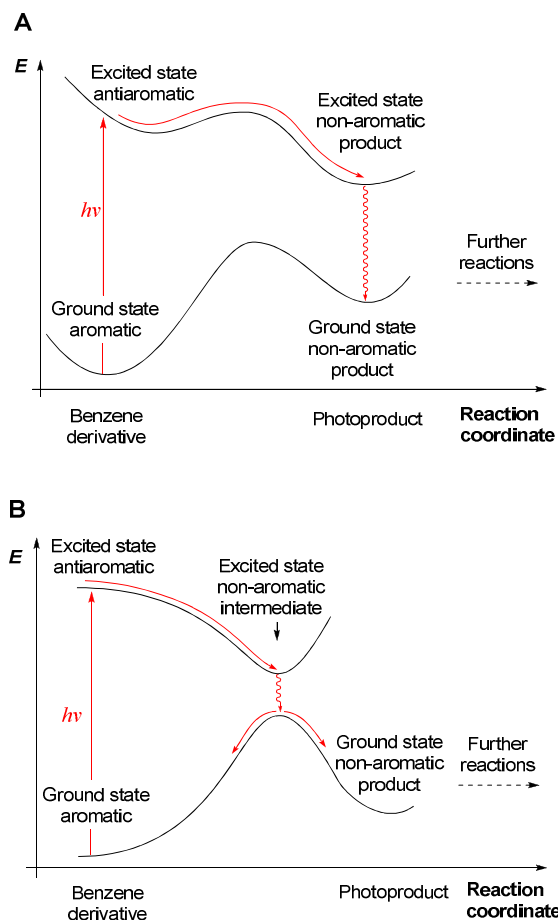
**Figure 1**: Schematic drawings showing how a destabilizing excited state antiaromatic (ESAA) character of a benzene derivative could function as a driver for photochemistry leading to photoproducts either through (A) an adiabatic or (B) a diabatic reaction mechanism.

## 2. Theoretical and computational analysis

As noted above, a series of theoretical and computational studies have been devoted to aromaticity and antiaromaticity effects in the lowest $\pi\pi^*$ excited states of [4*n*]- and [4*n*+2]annulenes, respectively.[1-11,38-40,42-52] Our present analysis is primarily focused on theoretical and computational studies of the excited state antiaromaticity of benzene (**1**). For a

more comprehensive treatise of theory and computations on the ES(A)A concept we refer to a previous review of ours.[12] Aromaticity and antiaromaticity in a photochemical context were first applied independently by Dewar and Zimmerman for the rationalization of allowed and forbidden pericyclic reactions, thermal as well as photochemical.[53-55] According to the Dewar-Zimmerman approach, allowed pericyclic reactions proceed over aromatic transition states while those that are forbidden are forced to go over transition states that are antiaromatic.

The concept of excited state (anti)aromaticity was first applied to structures that are minima on the excited potential energy surfaces (PES) by Baird in 1972.[1] He used PMO theory to show that the rule for aromaticity and antiaromaticity in the lowest $\pi\pi^*$ triplet state is opposite to what is given by Hückel's rule for the $S_0$ state. Baird's rule thus tells that benzene is antiaromatic in its $T_1$ state, and the qualitative derivation of this finding is displayed in Figure 2. In this analysis one forms triplet biradical benzene from two allyl monoradicals, and one considers the interaction between the various $\pi$-orbitals of the allyl radicals. Does the interaction lead to an overall stabilization or destabilization of the triplet biradical annulene when compared to two separate polyenyl radicals? To answer this question Baird considered two types of interactions: Type I interaction which is the interaction between the singly occupied $\pi$-MOs (SOMOs) of the two polyenyl radicals, and Type II interaction which is the interaction of the SOMO of one polyenyl radical with the doubly occupied and the empty $\pi$-MOs of the other polyenyl radical.
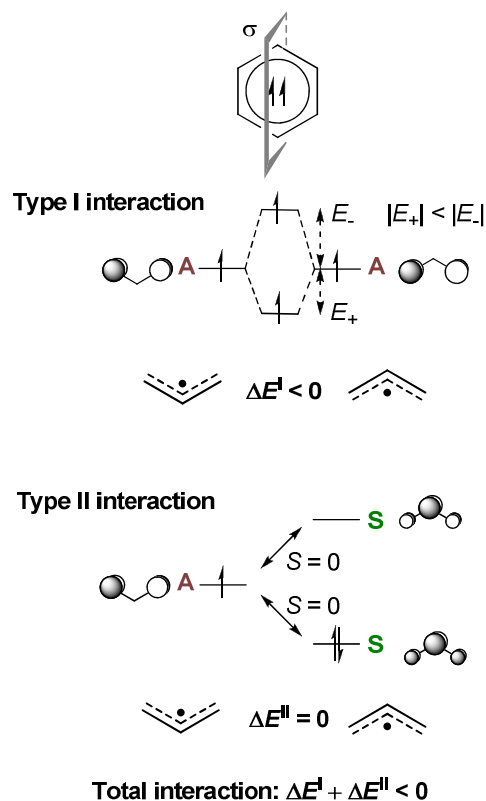
**Figure 2**: The Type I and Type II interactions between the $\pi$-MOs of two allyl monoradical fragments leading to triplet biradical benzene. For the Type II interaction only one of the two equivalent interactions is displayed. Fragment orbitals which are symmetric with regard to the bisecting mirror plane are labelled S and those which are antisymmetric are labelled A. A zero orbital overlap between fragment orbitals of different symmetries is denoted by $S = 0$.

The interaction strength is determined by the symmetry of the orbitals and orbital energy differences, and following from PMO theory, the out-of-phase (antibonding) interaction between two polyenyl radical $\pi$-MOs is more destabilized than the corresponding in-phase (bonding) interaction is stabilized, *i.e.*, $|E_+| < |E_-|$ (see Figure 2).[56] As triplet state benzene is constructed from two allyl radicals the two SOMOs have the same symmetry with respect to a common

mirror plane ($\sigma$) bisecting the two radicals, and this leads to a non-zero Type I interaction which is destabilizing as the two resulting $\pi$-MOs will each be singly occupied in the triplet state. The Type II interaction, on the other hand, is exactly zero because SOMO on one allyl radical fragment has opposite symmetry to the highest doubly occupied $\pi$-MO (HDOMO) and the lowest unoccupied $\pi$-MO (LUMO) on the other allyl radical (*i.e.*, orbital overlap $S = 0$). When Type I and Type II interactions are summed up the conclusion is that triplet state benzene is destabilized when compared to the two allyl radicals which represent the non-aromatic reference system.

Valence bond (VB) theory can also be used to qualitatively understand the reversal in the electron count for aromaticity and antiaromaticity in the $T_1$ state. Zilberg and Haas analyzed the first triplet state of [4$n$]annulenes with VB theory and concluded that "in the triplet, the most symmetric form can be maintained, since these two electrons [*i.e.*, the two unpaired same-spin $\pi$-electrons] cannot form a bond, losing their distortive power. Therefore, the system is now essentially an odd parity system, with an odd number of electron pairs. Such a system has a characteristic aromatic stabilization so that the lowest lying triplet is expected to have an aromatic character."[39] *I.e.*., in triplet state cyclooctatetraene (COT), with five $\pi_\alpha$-electrons and three $\pi_\beta$-electrons, there can only be three CC $\pi$-bond pairs leaving two $\pi_\alpha$-electrons unpaired. Hence, triplet state COT can be described as a Hückel-aromatic 6$\pi$-electron COT dication plus two non-bonding same-spin $\pi$-electrons. Now, this article is devoted to benzene in its lowest triplet and singlet excited states. The VB theoretical interpretation of [4$n$]annulenes in their lowest triplet states could be expanded to benzene if this compound is considered to be composed of a closed-shell 4$\pi$-electron benzene dication plus two additional non-bonding same-

spin $\pi$-electrons (Figure 3). The benzene dication in its lowest singlet state is Hückel-antiaromatic with, *e.g.*, a NICS(1)$_{zz}$ value of 27.7 ppm and a PDI value of 0.059.[57,58] As the benzene dication in the singlet state has an optimal $D_{2h}$ symmetric structure described as two allyl cation segments joined by two longer C-C bonds,[58] it is not surprising that one of the structures of triplet state benzene is of a similar diallylic form.
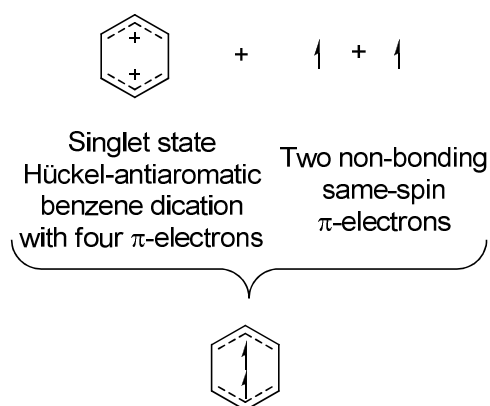


**Figure 3:** Schematic formation of triplet state benzene through the addition of two non-bonding $\pi_\alpha$-electrons to the Hückel-antiaromatic benzene dication in its lowest singlet state.

Indeed, the geometries of benzene in the $T_1$ and $S_1$ states are noteworthy. In the triplet state benzene lowers the symmetry to either of two structures (Figure 4); a quinoid ($^3$**1-Q**) and an antiquinoid ($^3$**1-AQ**) or diallylic structure, both having $D_{2h}$ symmetry. The $^3$**1-Q** is lower than than $^3$**1-AQ** by merely 0.7 kcal/mol, and the $D_{6h}$ symmetric structure which is the transition state for the interconversion is 2.5 kcal/mol above $^3$**1-Q** at MCSCF/6-31G(d) level.[59] In the $S_1$ state it has been found experimentally that benzene still has $D_{6h}$ symmetry but with CC bonds which are elongated to 1.432 – 1.435 Å.[60,61] Interestingly, the drive to these structural changes are also

notable in the extent of electron sharing between pairs of C atoms when benzene is calculated in

the $T_1$ and $S_1$ states at the hexagonal structure (*vide infra*).[8]
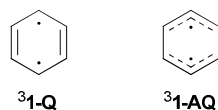


$^3$**1-Q**      $^3$**1-AQ**

**Figure 4**: The quinoid and antiquinoid structures of benzene in the $T_1$ state.

Computational assessment of aromaticity should ideally be performed with a selection of different aromaticity indices.[62] There are four types of (anti)aromaticity indices; geometry-based indices, energy-based indices, indices based on magnetic properties, and indices based on the electron density. For the triplet state aromaticity slightly more focus in previous computational studies seems to have been placed on probing the aromaticity of [4n]annulenes instead of the antiaromaticity of [4n+2]annulenes.

With regard to geometry-based indices none have been applied to the $T_1$ and/or $S_1$ states of benzene. However, as the parameters in the most frequently used geometry-based index, the HOMA index (Harmonic Oscillator Model of Aromaticity),[63] were derived for the $S_0$ state they should not be ideal for estimation of the aromaticity of excited states where bond lengths are longer simply due to the occupation of $\pi$-MOs with more nodes. Yet, if one calculates HOMA of $T_1$ benzene based on the antiquinoid (U)OLYP/6-311G(d) geometry a HOMA value of -0.545 results corresponding to antiaromatic character, and when calculated for the $S_1$ state based on the

experimental geometry ($D_{6h}$ with CC bond lengths of 1.432 Å)[61] one obtains a HOMA of 0.501 which corresponds to significantly reduced aromaticity.

The Hückel resonance energies (HREs) is the simplest energy-based measure that reveals a difference between annulenes in their electronic ground states versus their first $\pi\pi^*$ excited states. It should, however, be noted that the HREs are the same for the first singlet and triplet $\pi\pi^*$ states as multiplicity is not considered. Aihara used a characteristic polynomial to represent the localized structure of an annulene.[2] For each annulene and for each orbital topology (Hückel or Möbius) he found a change in the sign of the HRE when going from $S_0$ to the first $\pi\pi^*$ state, benzene no exception (Table 1). The same finding was made by Ilić et al. for the topological resonance energies (TREs) based on Hückel orbital energies.[3] Baird in his 1972 paper used the semiempirical NDDO method to compute Dewar resonance energies (DREs) in the $T_1$ state for the quinoid as well as the antiquinoid structures (Figure 4), and found them to be destabilized,[1] opposite to what is the situation for benzene in $S_0$ at the same level of computation.[64] More recently, Schleyer developed the isomerization stabilization energy (ISE) method so as to overcome perturbing influences such as strain in the computation of aromatic stabilization energies.[65] This method is applied to the methyl derivative of a certain compound, e.g., toluene instead of benzene (Figure 5). Yet, for toluene one finds a negative ISE in $S_0$ and positive ISE in $T_1$, although the values in $T_1$ are smaller in absolute sense than the ISE value in $S_0$.[9] No energy-based aromaticity index has to our knowledge been reported for benzene in the $S_1$ state.
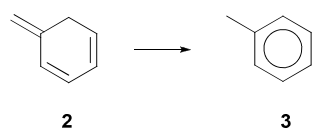


2                          3

**Figure 5**: The reaction used for determination of the isomerization stabilization energies of toluene (**3**) in the $S_0$ and $T_1$ states.[9,65]

**Table 1**: Values from various aromaticity indices for benzene in its $S_0$, $T_1$ and $S_1$ states.

| Aromaticity index | $S_0$ ($^1A_{1g}$) | $T_1$ ($^3B_{1u}$) | $S_1$ ($^1B_{2u}$) |
|---|---|---|---|
| HRE [a] | 0.273 | -0.692 | - |
| TRE [b] | 0.270 | -0.690 | - |
| DRE [c] | 21 | -16.4, -12.3 | - |
| ISE; $ISE_{corr}$ [d] | -33.2; -33.2 | 13.5; 16.9 | - |
| $\chi_\pi/\chi_\pi(S_0)$ [e] | 1.00 | -2.00 | -4.79 |
| $\chi_{iso}$ [f] | -59.33 | -6.16 | 2.43 |
| $\chi_{zz}$ [f] | -99.67 | 56.93 | 78.97 |
| $NICS(0)_{zz}$ [f] | -12.21 | 130.54 | 145.90 |
| $NICS(1)_{zz}$ [f] | -27.83 | 90.61 | 102.76 |
| $PDI^A$ [g] | 0.074 | 0.018 | 0.010 |
| $PDI^F$ [g] | 0.050 | 0.015 | 0.010 |
| $FLU^A$ [g] | 0.000 | 0.033 | 0.012 |
| $FLU^F$ [g] | 0.000 | 0.020 | 0.006 |
| $I_{ring}$ [g] | 0.0305 | 0.0027 | 0.0040 |
| $MCI$ [g] | 0.0435 | 0.0023 | 0.0041 |

| RCBV(ELF$_\pi$)[h] | 0.9065 | 0.144 | - |
| $\Delta$BV(ELF$_\pi$)[h] | 0.000 | 0.745 | - |

[a] Values from reference 2. [b] Values from reference 3. [c] Values from references 64 (S$_0$) and 1 (T$_1$).

[d] Values from reference 9. [e] Values from reference 4. [f] Values from reference 5. [g] Values from

reference 8. [h] Values from reference 6.

With regard to magnetically based aromaticity indices, Kataoka used a semiempirical Pariser-

Parr-Pople (PPP) SCF method to calculate the magnetic susceptibilities for the six excited states

of benzene (three singlet and three triplet states generated from the one-electron

HOMO→LUMO excitation).[4] The T$_1$ state was found to be markedly antiaromatic with a

magnetic susceptibility ratio ($\chi_\pi/\chi_\pi(S_0)$) of -2.00 when the magnetic susceptibility $\chi_\pi$ is compared

to that of the S$_0$ state. For the S$_1$ state the ratio was even more strongly suggestive of

antiaromaticity (Table 1). Karadakov examined the magnetic susceptibilities at CASSCF level,

both the isotropic and zz-tensor component.[5] Noteworthy, he wrote that $\chi_{zz}$ can be viewed as one

of the most sensitive aromaticity indices, and he found that it supports Baird's rule for both the

T$_1$ and S$_1$ states. The NICS values of benzene in the S$_0$, T$_1$ and S$_1$ states were also calculated at

CASSCF levels by usage of the GIAO method (Gauge-Independent Atomic Orbitals)[66], and also

the T$_1$ state was found to be highly antiaromatic. Interestingly, benzene in S$_1$ state displays NICS

values which are similar or higher than those of cyclobutadiene at its $D_{4h}$ symmetric S$_0$ state

structure for which NICS(0)$_{zz}$ and NICS(1)$_{zz}$ values of 145.9 and 88.1 ppm were calculated.[5]

Yet, a direct comparison of the NICS values of differently sized annulene rings should be

avoided as the NICS values depend on the size of the ring.[67]

For the electron density based aromaticity indices there exist three studies, and one of these deals with both $T_1$ and $S_1$ antiaromaticity. The $T_1$ state of benzene has $D_{2h}$ optimal structures ($^3$**1-Q** and $^3$**1-AQ**) and this is reflected already in the extent of electron sharing between pairs of C atoms at the $D_{6h}$ symmetric structure because the values for the two bonds are 1.429 e while the other four are 1.100 e at CASSCF(6,6) level.[8] The values of the *para*-delocalization index and the aromatic fluctuation index according to Fulton (PDI$^F$ ad FLU$^F$, respectively), the multicenter index (MCI), and the $I_{\text{ring}}$ index are all in line with Baird's rule and antiaromaticity of benzene in the $T_1$ state. From the ring-closure bifurcation values and the span in the bifurcation values of the $\pi$-contribution to the electron localization function (RCBV(ELF$_\pi$) and $\Delta$BV(ELF$_\pi$), respectively),[6] as well as from the non-degeneracy in the Hessian eigenvalues of the $\pi$-electron density and an elliptical shape of the anisotropy of this density, one can also conclude on an antiaromatic character in the $T_1$ state.[10] For the $S_1$ state, three of the four different types of electronic aromaticity indices (the PDI$^F$, $I_{\text{ring}}$ and MCI indices) indicate antiaromaticity.[8] However, the fourth index (the FLU index) reveals only a slight increase and tendency towards antiaromaticity (the FLU$^F$ of $S_1$ state benzene is 0.006, while for cyclobutadiene at its $D_{2h}$ symmetric structure in $S_0$, representing an antiaromatic prototype, it is 0.036).

With regard to the $S_1$ state of benzene its antiaromaticity has only been examined by magnetic and electron density based aromaticity indices. Furthermore, the calculations have been performed at CASSCF level, *i.e.*, effects of dynamic electron correlation on the $S_1$ state antiaromaticity have not been properly considered. Yet, both the NICS and $\chi_{zz}$ values from Karadakov's CASSCF calculations and the relative $\chi_\pi$ value from Kataoka's PPP calculations suggest a stronger antiaromaticity for $S_1$ than for $T_1$. In summary, there are significant support from a range of different theoretical and computational studies that benzene is antiaromatic in its

lowest excited states, the $T_1$ and $S_1$ states. In the next part we will review the photophysics and photochemistry of benzene itself, and then, place emphasis on the different photoreactions of benzene derivatives. In our view, it is in the photochemistry of various benzene derivatives where the $S_1$ and $T_1$ antiaromaticity of the benzene ring, its Mr. Hyde character, reveals itself most clearly.

### 3.  Photophysics and photochemistry of benzene

A single electron HOMO→LUMO excitation from the filled doubly degenerate $e_{1g}$ orbitals to the vacant doubly degenerate $e_{2u}$ orbitals of benzene generates six electronically excited states; three singlet states ($^1B_{2u}$, $^1B_{1u}$ and $^1E_{1u}$) and three triplet states ($^3B_{2u}$, $^3B_{1u}$ and $^3E_{1u}$).[68] A variety of quantum chemical calculations on the lowest excited states have been reported, yet, in all computations the order in energy is uniformly given as $^1B_{2u} < {}^1B_{1u} < {}^1E_{1u}$ for the three singlet states and $^3B_{1u} < {}^3E_{1u} < {}^3B_{2u}$ for the triplet states.[69-74] It is remarkable that both the $S_1$ state and the $T_1$ state in benzene are at higher energies (vertical transitions at 4.90 and 3.95 eV)[75,76] than in the isomeric pentafulvene (vertical transitions at 2.35 and 3.45 eV, respectively)[77,78]. This fact reflects the aromatic stabilization of benzene in the $S_0$ state as it is 1.50 eV lower in energy than fulvene at B3LYP/6-31G(d) level.[79] Yet, from the $S_0$ energy difference and the vertical excitation energies one can tentatively conclude that benzene and fulvene are approximately isoenergetic in their $S_1$ states.

The excited state dynamics of benzene is still a vibrant research area as revealed by the recent studies on the so-called "channel 3" region.[80-83] It has earlier been observed that the fluorescence quantum yield ($\Phi_F$) went down drastically if the excitation energy was higher by 0.37 eV (3000

cm$^{-1}$) than the energy needed for the 0-0 transition.[84,85] The non-radiative decay *via* channel 3 (channels 1 and 2 being UV fluorescence and intersystem crossing (ISC), respectively) has recently been confirmed through UV-laser-induced IR-fluorescence (UV-LIIRF) excitation spectroscopy and dispersed UV-LIIRF spectroscopy.[83] It was then found that when benzene is excited with irradiation above the onset of channel 3 the IR fluorescence yield is higher than when it is excited below this limiting energy value, schematically shown in Figure 6. Thus, photochemical isomerization leading away from the antiaromatic $S_1$ state of benzene is only efficient in an energy window framed by the 0-0 transition and the onset of channel 3.
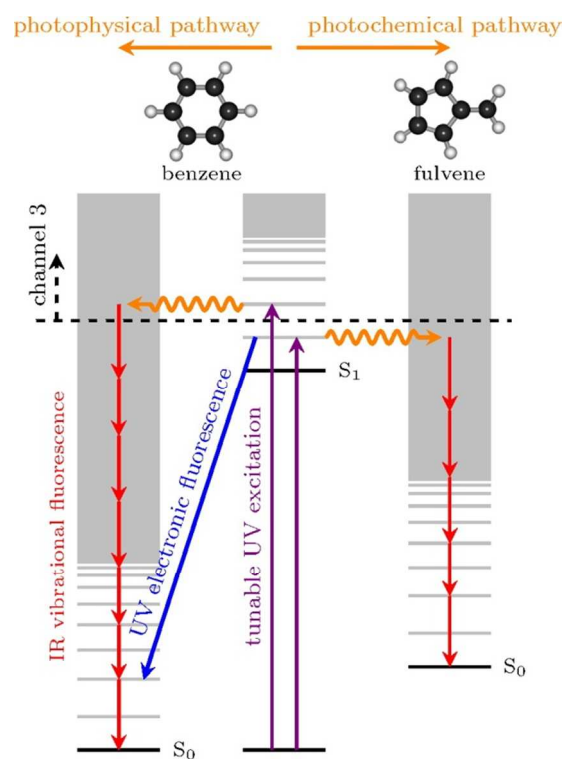


**Figure 6**: Jablonski diagram summarizing the radiative and non-radiative processes of benzene above and below the onset of channel 3 observed by Féraud *et al.* (ref. 83). Gray areas represent the vibrational states, wave lines the non-radiative processes, violet lines the tunable UV

excitation, blue arrows the UV electronic fluorescence, and red arrow the IR emission. Adapted

with permission from ref. 83. Copyright 2014 American Chemical Society.

As concluded by Aihara, benzene in its $S_1$ state undergoes photorearrangements,[2] and the

products upon excitation to the strongly antiaromatic $S_1$ state are benzvalene (**5**) and fulvene (**6**)

(Scheme 1). However, the quantum yields for formation of these compounds are low ($\Phi = 0.03$

and 0.012, respectively, when excited at 254 nm).[86,87] It has been found through CASSCF

calculations that the only minimum on the $S_1$ PES of benzene is of $D_{6h}$ symmetry corresponding

to the *anti*-Kekulé benzene valence bond isomer.[88,89] Progressing from this minimum in the $S_1$

state along the reaction coordinate, a transition state was found at 1.00 eV (23 kcal/mol) higher

energy, leading to the formation of a species with a prefulvene-like geometry at the conical

intersection (CI) where degeneracy of the $S_0$ and $S_1$ states is observed. Through this CI,

prefulvene (**4**) either leads back to benzene or it leads on to benzvalene, both in $S_0$.[88] The latter

two isomerizations are almost barrierless. On the other hand, the formation of fulvene *via* **4** is

thermal and requires [1,2] H-shift as well as breaking of one CC bond, and this explains the

lower quantum yield for the formation of fulvene as compared to benzvalene.[89] More recently, Li

*et al.* showed through high-level CASSCF//CASPT2 computations that the $S_1/S_0$ intersection

space of benzene is characterized by two $S_1/S_0$ seam branches which are connected by a seam

segment of $C_s$ symmetry.[90] It was shown that the global energy minimum of the seam is the half-

boat shaped intersection leading to the prefulvenic intermediate, which was previously described

by Palmer *et al.*[88] More recent computational studies at the CASSCF(6,6)/cc-pVDZ level

combined with VB theory have shown that the conical intersection seam for benzene exhibits a

very rich topology, and 12 permutational isomers of the minimum energy prefulvene-like CI

were recognized.[91] To conclude, a series of different channels are available for benzene in the $S_1$

state. The barrier that should be overcome for photochemistry is, however, rather high (23

kcal/mol) for photochemistry to be competitive with photophysics. With substituents at the

benzene ring this changes as new reaction channels are opened.
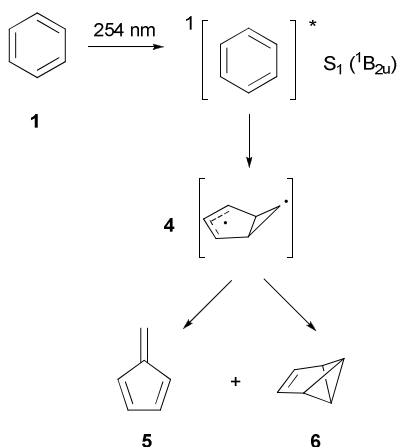


**Scheme 1**

## 4.  Photochemistry of styrene and other [4*n*+2]annulenyl olefins

The impact of ESAA and the struggle of the excited molecule to attenuate or alleviate this

destabilization, as shown in Figure 1, is most apparent in various benzene derivatives that are

able to undergo photochemistry rather than photophysics. It should, however, be remarked that

the concept of ESAA alleviation is a qualitative tool, and an actual photochemical process

leading from the excited benzene derivative to product is certainly more intricate involving

conical intersections and regions that allow for intersystem crossings along the reaction

coordinate. Yet, consideration of effects which involve loss of antiaromaticity (or gain of

aromaticity) along a photochemical reaction path can be helpful in the rationalization of a

photochemical reaction mechanism. In this section we discuss photoreactions of [$4n+2$]annulenyl olefins and how they can be influenced by ESAA. Focus is put on the triplet state olefin bond twist (*cf. Z/E*-photoisomerization) of styrenes as well as the photoaddition reactions of alcohols and water to styrenes.

It was reported by Ottosson and co-workers, based on DFT and CASPT2//CASSCF computations, that $T_1$ state *Z/E*-photoisomerizations of aryl and annulenyl-substituted olefins are influenced by (anti)aromaticity changes along the $T_1$ PES.[92-94] Based on those computations it was concluded that the structure with the highest substituent aromaticity (Baird-aromaticity or Hückel-aromaticity) corresponds to the minimum on the $T_1$ PES. As the shape of the $T_1$ PES is connected to the isomerization mechanism, adiabatic or diabatic,[95] (anti)aromaticity should have clear effects on the photochemistry. Indeed, the site of the triplet excitation in an annulenyl-substituted olefin is closely connected to triplet state aromaticity or antiaromaticity. The obvious substituent which will adopt a triplet state aromatic character is the cyclobutadienyl substituent, and computations reveal that vinylcyclobutadiene (**7**) in its $T_1$ state has the triplet biradical character fully localized to the ring, which accordingly is markedly Baird-aromatic (Figure 7A). Upon twist of the olefinic C=C bond to a structure where the planes at the two sp$^2$ carbon atoms are perpendicular to each other (the $^3$p* structure) one radical is forced to localize to the $\beta$-carbon and the Baird aromaticity of a triplet biradical cyclobutadienyl ring is lost.[93] This aromaticity loss comes with a raise in energy.
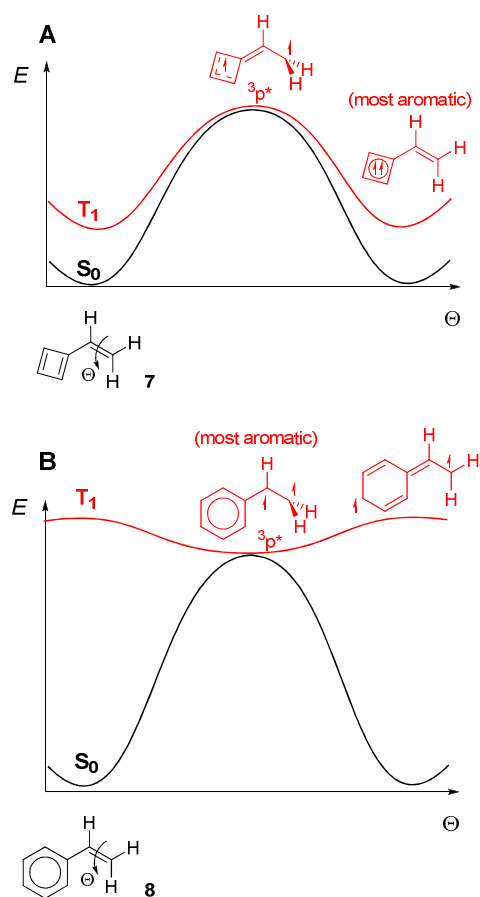
**Figure 7**: Schematic profiles of the $S_0$ and $T_1$ PESs for twist about the olefinic C=C bond of (A) vinylcyclobutadiene and (B) styrene, and with the most aromatic structures on the $T_1$ PESs marked.

A phenyl substituent which instead becomes $T_1$ state antiaromatic leads to the opposite class of olefins, represented by styrene as a prototype (Figure 7B). With an excited state antiaromatic benzene ring this latter olefin is prone to structural rearrangements in the $T_1$ state that alleviate its ESAA, and one such rearrangement is twist about the olefinic C=C bond to the $^3p^*$ structure. Computations using a range of different aromaticity indices, *e.g.*, NICS, HOMA, and properties of the $ELF_\pi$, all support that Baird-antiaromaticity is reduced, or alternatively, Hückel-

aromaticity is regained.[93,94] The $^3$p* structure of styrene is therefore best described as a 1,2-biradical localized to the olefin bond and a 6π-electron closed-shell Hückel-aromatic phenyl substituent (resonance structure **8-IIa**, Figure 8), in line with the reported description of Caldwell and Zhou.[96]

The findings can be generalized because olefins with a set of different [4*n*]annulenyl substituents were found to have very high energy barriers on the T$_1$ PES for twist about the CC bond whereas olefins with [4*n*+2]annulenyl substituents were found to have minima or shallow maxima at the $^3$p* structures.[93] Moreover, the shape of the T$_1$ PES for olefin C=C twist can be changed gradually between the two extremes through the degree of (anti)aromaticity of the annulenyl substituent; one extreme corresponds to the complete localization of the excitation to the olefin bond, the other corresponds to complete excitation localization to the substituent.[97] As the excitation localization affects the shape of the T$_1$ PES it also affects the mechanism of the *Z/E*-photoisomerization (diabatic or adiabatic).[95,98,99]
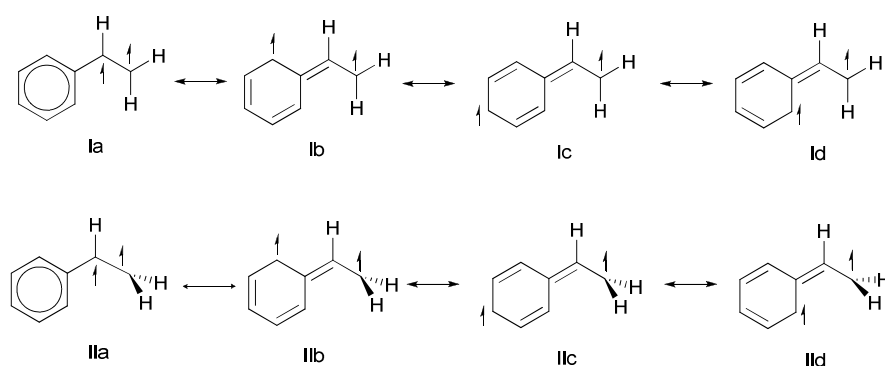


**Figure 8**: Resonance structures of styrene in the planar and perpendicularly twisted ($^3$p*) olefin structures.

As seen above, a relief in the T$_1$ antiaromaticity of the benzene ring is linked to the shape of T$_1$ PES of C=C bond twist in styrene. Such ESAA alleviation may also explain the mechanisms of

other photoreactions of styrenes. For example, variously substituted styrenes undergo photoadditions of alcohols or water to the olefinic bond, in contrast to what is the situation in the $S_0$ state where the compounds are unreactive. Their photoreactivity is connected to the polarization that styrene derivatives display in their planar $T_1$ or $S_1$ state. Wan *et al.* reported on anti-Markovnikov addition of water and alcohols to 3-nitrostyrene (**9**) in its $T_1$ state.[100] The photoaddition of water or MeOH proceeds *via* a planar reverse-polarized $T_1$ state (Scheme 2), and the polarization at this geometry can tentatively be viewed as a mode of the benzene ring in $T_1$ to attenuate the antiaromatic character it receives upon excitation. As a result, nucleophilic attack of water or alcohols takes place at the $\beta$-carbon, leading to a nitrobenzyl carbanion intermediate. Subsequent protonation gives the anti-Markovnikov addition products **10** (Scheme 3, reaction A).
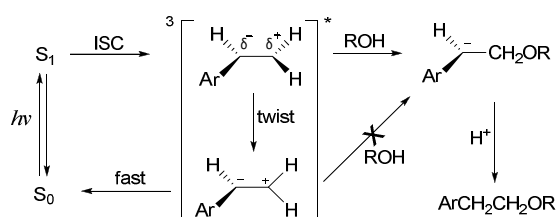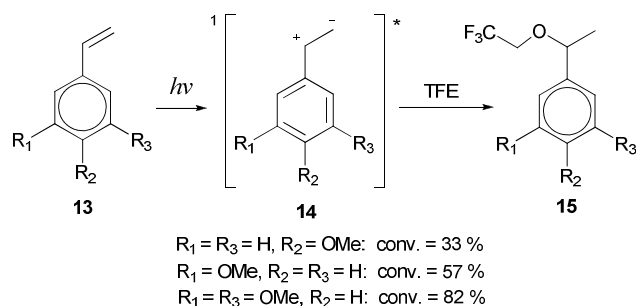


**Scheme 2**

Experimental support for the photoaddition of water and alcohols at the planar $T_1$ structure is provided by the behavior of 5-nitroindene **11** which also undergoes photoaddition of water and alcohols to give the anti-Markovnikov products **12**.[99] Noteworthy, **11** undergoes these photoadditions much more efficiently than non-cyclic 3-nitrostyrenes such as **9** because twisting about the olefinic C=C bond leads to the stabilized $^3$p* structure which rapidly deactivates to $S_0$ through radiationless intersystem crossing without addition of ROH. Since **11** is unable to attain the twisted structure the competing deactivation through $^3$p* is blocked and the nucleophilic

attack of alcohol becomes more favored. It is widely known that "locked" phenylcycloalkenes, *i.e.*, olefins which are structurally modified to prevent C=C bond rotation, exhibit increased $\Phi_F$ [101] as well as high triplet state lifetimes.[102] Additionally, they can also undergo facile photoaddition of alcohols, particularly MeOH.[103]
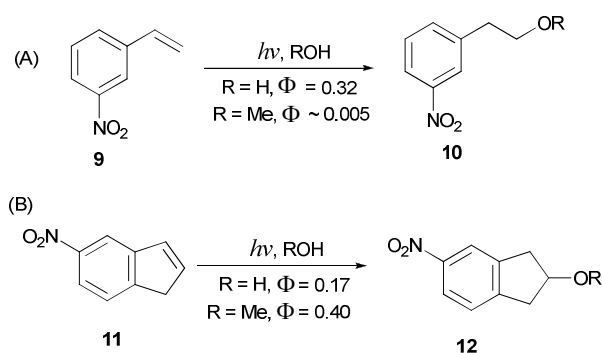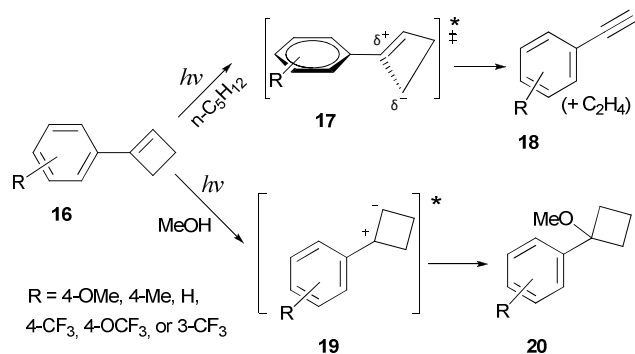


**Scheme 3**

Photoadditions of water and alcohols can also be performed with styrene derivatives that possess electron donating substituents (*e.g.*, methoxy groups) at the phenyl ring.[104-106] Yet, in these cases the photoadditions are considered to proceed *via* a polarized $S_1$ state, and the products are mainly Markovnikov photoadducts (Scheme 4), in contrast to the "anomalous" anti-Markovnikov photoadditions of the 3-nitrostyrene arising from a reverse-polarized $T_1$ state. Still, for both electron-deficient and electron-rich styrenes photoadditions occur through their planar $T_1$ or $S_1$ state structures.

R$_1$ = R$_3$ = H, R$_2$ = OMe:  conv. = 33 %
R$_1$ = OMe, R$_2$ = R$_3$ = H:  conv. = 57 %
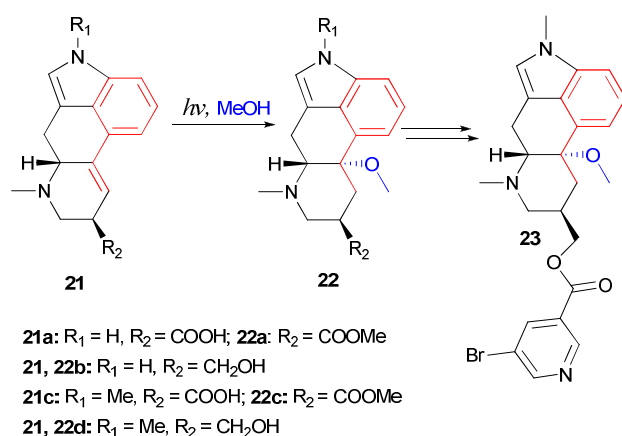R$_1$ = R$_3$ = OMe, R$_2$ = H:  conv. = 82 %

**Scheme 4**

1-Phenylcyclobutenes belong to the class of "locked styrenes". Leigh and Postigo found that these compounds when irradiated undergo [2+2] photocycloreversions leading to phenylacetylene and ethylene.[107] Yet, in presence of methanol they readily undergo alcohol photoaddition whereby photocycloreversion is surpressed (Scheme 5). The photoaddition of MeOH takes place in the S$_1$ state, and the MeOH photoadducts are Markovnikov products isolated in high chemical yields (75-85 %). The variation in yield is attributed to the different ability of carbocation stabilization depending on the substituent. The highest yields of **20** where observed when R = 4-OMe and 4-Me. The nature of the phenyl substituents can affect both the $\Phi_F$ as well as the MeOH photoaddition quantum yields ($\Phi_{MeOH}$). Going from electron donating to electron withdrawing substituents leads to increased $\Phi_F$ and decreased $\Phi_{MeOH}$ values. The latter effect is associated with the ability of electron donating substituents to provide electron density to the carbocation, facilitating nucleophilic attack ($\Phi_{MeOH}$ = 0.12 - 0.13 for electron donating and $\Phi_{MeOH}$ < 0.05 for electron withdrawing substituents). Such an effect for 1-phenylcyclobutenes is only possible in their planar S$_1$ structures, and therefore, the polarization which facilitates the photoaddition can tentatively be seen as a mode for ESAA relief of the benzene ring at the planar styrene structure.

**Scheme 5**

The photoaddition of MeOH to styrene derivatives has also found an industrial application. Lysergic acid, **21a**, which represents the basic skeleton of ergot alkaloids, undergoes stereoselective photoaddition of MeOH (Scheme 6).[108] This photochemical step is crucial as the methoxylated photoproduct **22c** is the precursor of compounds of great pharmaceutical interest such as nicergoline (**23**; [(8β)-10-methoxy-1,6-dimethylergolin-8-yl]methyl 5-bromopyridine-3-carboxylate), a drug used to treat several brain diseases, *e.g.*, senile dementia.[109] In the first step the photoinduced stereoselective addition of MeOH to **21c** results in the formation of the adduct **22c** (as a 9:1 mixture of diastereoisomers), which in a few steps leads to nicergoline (**23**).[110,111] The photoaddition of MeOH to the styrene-type olefinic bond (marked red, Scheme 6) is catalysed by $H_2SO_4$ under exclusion of dioxygen.



**21a:** $R_1$ = H, $R_2$ = COOH; **22a:** $R_2$ = COOMe
**21, 22b:** $R_1$ = H, $R_2$ = CH$_2$OH
**21c:** $R_1$ = Me, $R_2$ = COOH; **22c:** $R_2$ = COOMe
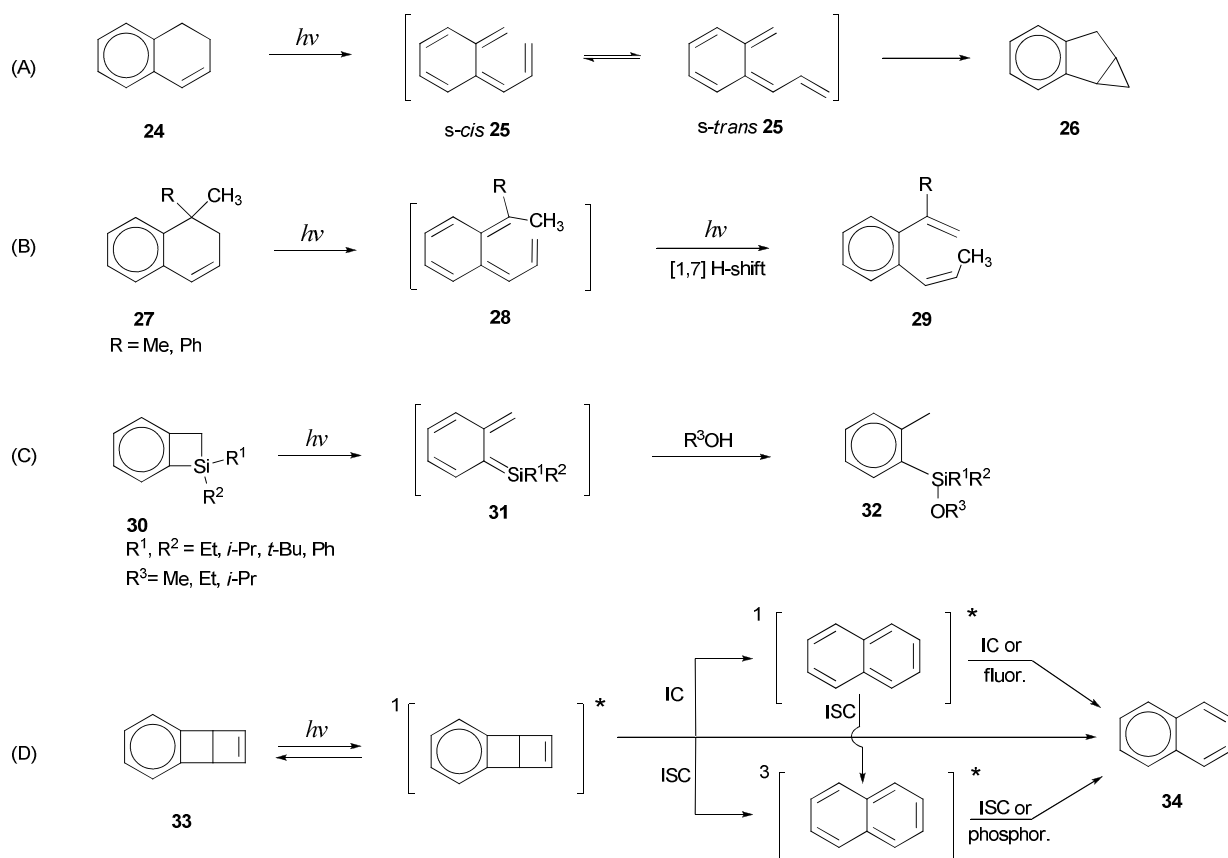**21, 22d:** $R_1$ = Me, $R_2$ = CH$_2$OH

**Scheme 6**

## 5. Photochemical formation of *ortho*-xylylenes

Photorearrangements of benzene derivatives leading to *o*-xylylene derivatives is a further reaction path that corresponds to an ESAA alleviation of an excited benzene ring. The formation of *o*-xylylene derivatives through various methods and their use in organic synthesis have been discussed in depth in an earlier review.[112] Herein, we exclusively review their formation through photochemistry. We begin by considering photochemical *o*-xylylene formation from precursors which are pure hydrocarbons or organosilanes with single saturated Si atoms, *i.e.*, molecules with no other chromophores than π-conjugated molecular segments containing a benzene ring. Because of their benzenoid chromophores these photoreactions should be strongly linked to the $S_1$ (and $T_1$) antiaromatic character of the benzene ring. Indeed, several of these compounds are conformationally locked styrenes, and thus connect and expand on the photochemistry reported in the previous section. Subsequently, we regard benzene derivatives which in addition to the benzene chromophore have substituents with lone-pairs and/or separate molecular segments which also are π-conjugated. Yet, despite these additional structural features their photochemistries should be dominated by the benzene chromophore. Its ESAA character should initiate photorearrangements to the *o*-xylylenes observed following either an adiabatic or diabatic mechanism (Figure 1).

A first example of photochemical formation of *o*-xylylene is the C-C bond cleavage of 1,2-dihydronaphthalene **24** resulting in the transient **25** (Scheme 7, reaction A).[113] This species after s-*cis*/s-*trans* isomerization leads to benzobicyclo[3.1.0]hexene **26** in high chemical yield (92 %).

The involvement of the transient s-*cis* and s-*trans* rotamers of **25** was concluded after the case of

hydrogen migration could be eliminated through experiments with deuterated samples. The

methyl substituted 1,2-dihydronaphthalene derivatives **27** undergo similar C-C bond cleavages

resulting in the transient *o*-xylylenes **28**, which after [1,7] sigmatropic H-shifts lead to the stable

products **29** (Scheme 7, reaction B).[114] Similarly, Kang *et al.* reported that the

benzosilacyclobutenes **30** undergo photochemical Si-C bond cleavages resulting in intermediate

*o*-silaquinone methides **31**, trapped by alcohols to yield the (dialkyl)alkoxy-*o*-tolylsilanes **32**

(Scheme 7, reaction C).[115] On the other hand, if the reaction between alcohols and **30** was carried

out in the $S_0$ state it progressed sluggishly. Furthermore, the photochemical conditions with

dioxygen present gave the same result, which should suggest that there was no quenching of a

triplet by dioxygen. Moreover, 1,4-Dewar-naphthalene (**33**) undergoes photoinduced valence

isomerization to naphthalene (**34**) according to Wallace and Michl (Scheme 7, reaction D).[116]

This reaction commences with the excitation of **33** to its $S_1$ state. Experiments in solid $N_2$

matrices at 10 K indicated that from the $S_1$ state, **33** can either return back to its $S_0$ state through

fluorescence or progress to naphthalene *via* ring-opening. The latter photochemical process can

occur through different paths *via* the $S_1$ or $T_1$ states of **33** (Scheme 7, reaction D), and should be

considered as a striving for reduction of the ESAA of the benzene ring of **33**.

(A)   24   s-*cis* 25   s-*trans* 25   26

(B)   27
R = Me, Ph
28   [1,7] H-shift   29

(C)   30
R$^1$, R$^2$ = Et, *i*-Pr, *t*-Bu, Ph
R$^3$= Me, Et, *i*-Pr
31   R$^3$OH   32

(D)   33   34

**Scheme 7**

Apart from C-C or Si-C bond scissions, photorearrangements leading to *o*-xylylenes that involve

migrations have also been reported. *E.g.*, hydrocarbon **35** undergoes hydrogen and phenyl

migration upon photoexcitation (Scheme 8, reaction A).[117-119] The indane derivative **35** is thus

transformed to the unstable isoindane **36**, which evolves in the $S_0$ state to **37**, isomeric to the

reactant **35**. The formation of the unstable *o*-xylylene intermediate **36** has been confirmed

through NMR spectroscopy at -70 °C. A final example of a photoreaction in a pure hydrocarbon

leading to an *o*-xylylene, and which could be viewed as an ESAA alleviation, is the

photochemically induced antarafacial [1,5] sigmatropic H-shift in compound **38** with R$^4$ = Ph,

reported by Pratt (Scheme 8, reaction B).[120] This compound adopts a non-planar conformation in

order to reduce steric congestion, and this conformation facilitates the photochemical antarafacial

[1,5] sigmatropic shift which results in the transient *o*-xylylene **39**. Pratt trapped this intermediate through a Diels-Alder reaction with maleic anhydride, yielding compound **40**. Hornback and Barrows several years after reported that photochemical [1,5]sigmatropic shift is also possible for alkylsubstituted derivatives **38** ($R^4$ = Me or Et, Scheme 8, reaction B).[121] Upon irradiation of the aforementioned pure hydrocarbons the transients *o*-xylylene derivatives **39** were trapped *via* Diels–Alder reaction with maleic anhydride. Interestingly, the formation of **39** from **38** with $R^4$ = Me or Et was not observed under sensitized conditions using xanthone as triplet sensitizer, which implies that the photoreaction occurs in the $S_1$ state.
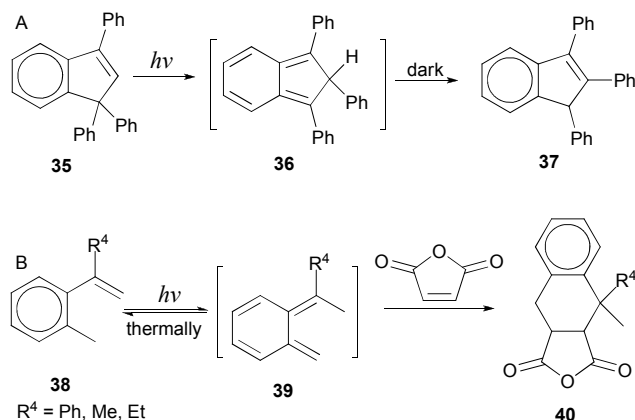


**Scheme 8**

Taken together, the photoreactivity of benzene derivatives **24**, **27**, **30**, **33**, **35** and **38** should reflect their effort to reduce the $S_1$ antiaromatic character of the benzene ring. It is particularly noteworthy that the reactants in all reactions of Schemes 7 and 8 possess no other chromophores than the π-conjugated molecular segments. Also all reactants, except **30** which has a single $sp^3$ hybridized Si atom, are pure hydrocarbons with styrene segments.

A compound with heteroatoms with lone-pairs, but with the chromophore of the lowest excitations still localized at the $\pi$-conjugated styrene segment, is **41**. Feast and Preston reported that this perfluorinated molecule undergoes a sigmatropic F-shift upon irradiation at $\lambda = 254$ nm, a photochemical process which requires the cleavage of a strong C-F bond in order to achieve ESAA alleviation (Scheme 9).[122] The reactive intermediate **42** was trapped by ethylene to yield the isolated compound **43**.
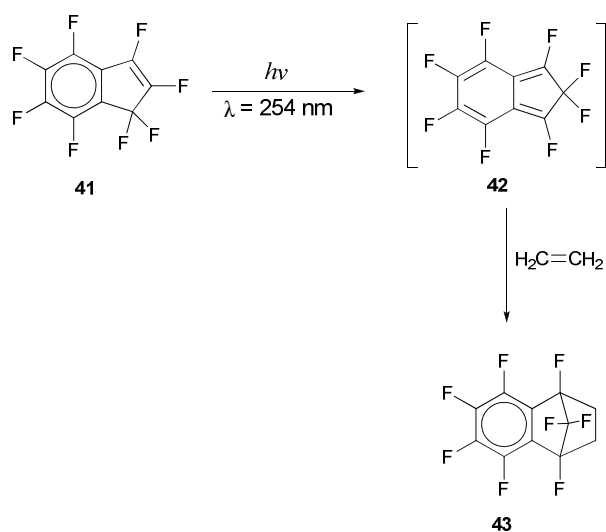


**Scheme 9**

In addition to **41**, there are also other reactants with substituents or functional groups with lone-pairs (Schemes 10-17), and which upon irradiation give *o*-xylylenes. Yet, despite these lone-pairs the benzene ring is an integral part of the chromophores in these molecules. The benzocyclobutenols **44** are the first examples of such species.[123] Disrotatory ring-opening in **44** is feasible photochemically, whereas conrotatory opening, which would occur thermally, is tough and would lead to compounds with *trans*-unsaturation. The photolysis of **44** led to the benzocycloalkenones **46** in moderate chemical yields (21 − 48 %). Attempts to trap the *o*-xylylene intermediates **45** through Diels-Alder reactions failed but photolyses in the presence of

dioxygen gave the hydroxyperoxides **47**. Nevertheless, trapping through reaction with $O_2$ cannot

provide insights on the nature of the intermediates. However, the results of the photolyses of **44**

in MeOD and $CD_3OH$ led to the conclusion that dienols **45** (*o*-xylylene derivatives) are the

intermediates formed upon irradiation of **44**, and with these experiments they could eliminate the

assumption that the reaction proceeds *via* diradical intermediates. Furthermore, photolyses of

methylethers **48** yielded the enol ethers **50** (Scheme 10, reaction B). Both reactions A and B of

Scheme 10 proceed in the $S_1$ state as no reaction in presence of benzophenone as triplet sensitizer

was observed.
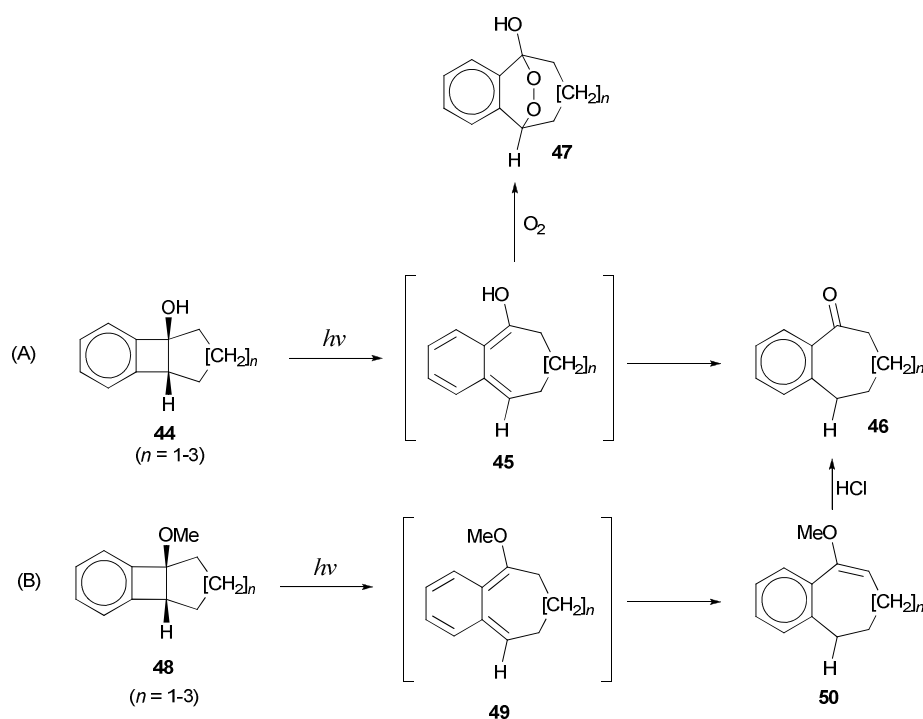


**Scheme 10**

Sakamoto and Ishikawa reported that benzodisilacyclobutene **51** undergoes thermal Si-Si bond

cleavage leading to the very reactive *o*-disilaxylylene derivative **52**.[124] The latter readily

dimerizes to yield **54**, or alternatively, in the presence of various acetylenes which act as *o*-xylylene trapping agents, forms the products **55** (Scheme 11). Interestingly, upon irradiation at λ = 254 nm, using a Vycor filter blocking shorter wavelengths, **51** neither undergoes dimerization nor reacts with alkyne trapping agents but instead yields **56** (Scheme 11). This observation was rationalized by the authors as a photoinduced homolytic Si-Si σ-bond scission giving the biradicaloid intermediate **53**. However, as the irradiation was performed at λ = 254 nm it is unlikely that the Si-Si bond chromophore absorbs because the longest absorption wavelength found for a hexaalkyl substituted disilane (λ = 206 nm) is reported for (*t*Bu)₃Si-Si(*t*Bu)₃ having an extremely elongated Si-Si bond.[125] Moreover, the σ and σ* orbitals of the Si-Si bond are orthogonal to the benzene π-orbitals, *i.e.*, the orbital interaction between these molecular segments should be negligible. Instead, the photochemical results should stem from ESAA alleviation upon excitation of the benzene ring of **51**. Similar to benzomonosilacyclobutene **30**,[115] the excitation of **51** could result in ring-opening and formation of the corresponding disilaquinone methide derivative, and the reactive biradical **53** could also derive from the disilaquinone methide derivative.
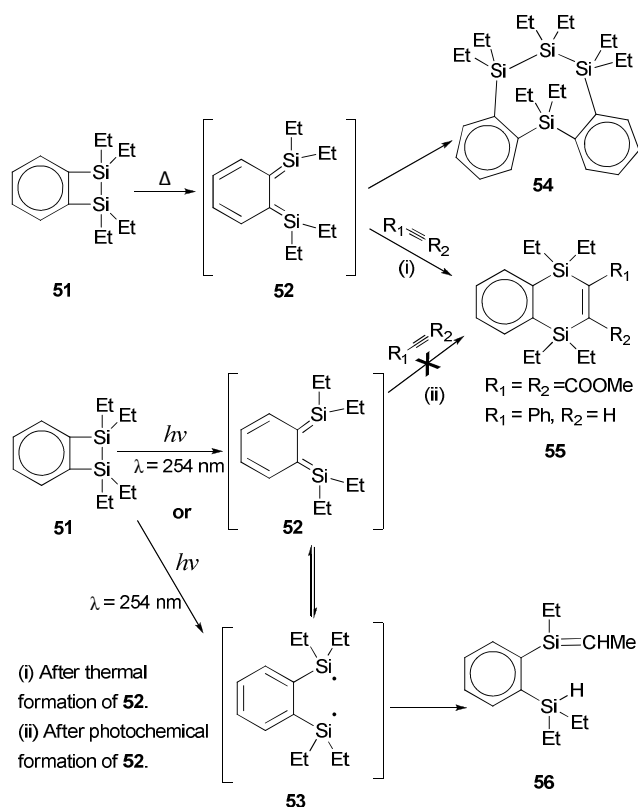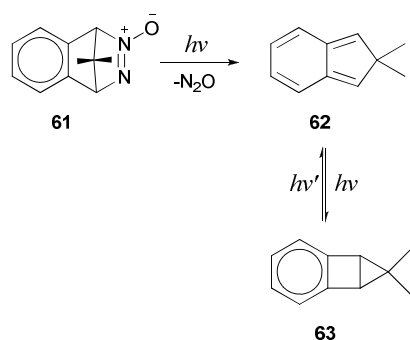
**Scheme 11**

A further example of photochemical production of an *o*-xylylene derivative is the photolysis of

*o*-trifluoromethylaniline **57** reported by Seiler and Wirz (Scheme 12).[126] Upon irradiation of **57**,

the formation of the reactive *o*-xylylene intermediate **58** was observed spectroscopically. For the

formation of the latter, the splitting of a C-F bond (the strongest single bond to carbon) is

required. This fact should reflect the force in the drive of the excited benzene ring to alleviate its

ESAA. Subsequently, this derivative is hydrolysed to anthranilic acid **60** *via* the intermediate

anthranoylfluoride **59**. As further reported by the same authors, *o*-trifluoromethylphenol also

undergoes photolysis *via* a corresponding *o*-xylylene intermediate.[127] It was concluded that these

photoreactions first involve a ππ* excited singlet state, which upon C-F bond elongation crosses

with a dissociative πσ* state.[126]
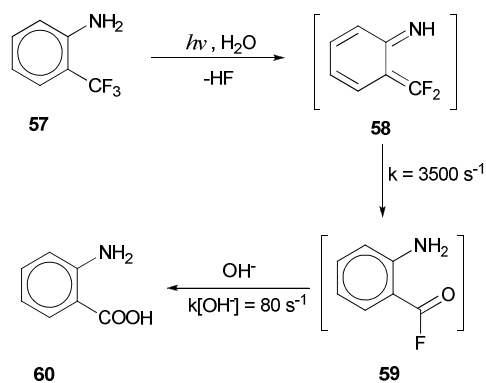
**Scheme 12**

The photoextrusion of a small molecule, and simultaneous photochemical formation of an *o*-xylylene, should be another route for ESAA alleviation of an excited benzene derivative. A first such case is compound **61**, which upon irradiation at $\lambda = 254$ nm undergoes expulsion of $N_2O$ and formation of the isoindene derivative **62** as a result of the local excitation of the benzene ring (Scheme 13).[128] The same photoreaction also occurs upon irradiation at $\lambda > 285$ nm, but then through excitation of the azoxy group. Interestingly, the strongly fluorescent isoindene derivative **62** is stable upon UV-irradiation in a rigid glass at 77 K. It can photoisomerize to the benzofused bicyclic product **63**, but this reaction requires thermal activation and **63** readily photorearranges back to **62** (Scheme 13). Consequently, *o*-xylylene **62** is accessible both by the photoreaction of the benzene derivative **61** and by the photorearrangement of **63**. It is noteworthy that **63** has some resemblance with **44** and **48**, yet, in the latter two cases the cycloalkanes fused to benzocyclobutene are larger than the cyclopropane ring in **63**. The photochemical opening of the benzocyclobutene ring is therefore not necessarily assisted by ring strain within the additional cycloalkane ring.
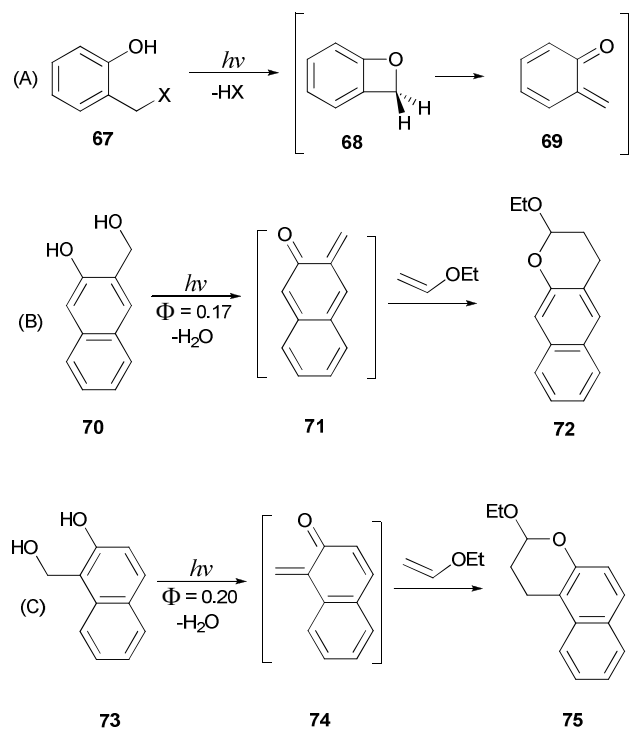
**Scheme 13**

In a similar manner, compound **64** undergoes ethylene photoextrusion when irradiated at $\lambda = 254$

nm at 77 K in a 2-methyltetrahydrofuran matrix to give dicyanoisobenzofulvene **65** (Scheme 14),

also an *o*-xylylene.[129] Here it should be noted that the expulsion of ethylene through thermolysis

or pyrolysis has been accomplished for compounds similar to **64** having substituents other than

cyano groups, but these thermal reactions required heating for one week at 120 $^{\circ}$C, or

alternatively, flow pyrolysis at 600 $^{\circ}$C.[130] Clearly, in the $S_0$ state the thermal extrusion of an

ethylene molecule from **64** and formation of **65** involves loss of Hückel $S_0$-aromaticity. In

contrast, upon local excitation of the benzene ring of **64** to its $S_1$ antiaromatic state the benzene

ring alleviates its ESAA through formation of the transient isobenzofulvene. The formation of **65**

as an intermediate is evident through a deep red-purple coloration of the matrix attributed to the

characteristic absorption maxima of dicyanoisobenzofulvene.[131] A quick decoloration and

formation of dimer **66** was observed when the temperature was raised.
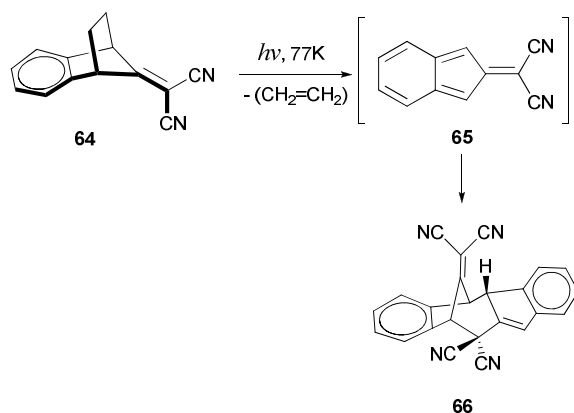
**Scheme 14**

Carbon monoxide photoextrusion in 2-indanones, which results in the formation of *o*-xylylene

derivatives, has been reported by Starr and Eastman.[132] Even though these

photodecarbonylations are considered as Norrish Type-I reactions, the assistance of benzene ring

ESAA alleviation along the reaction paths toward the products should also be taken into account.

Photochemical split-off of a water, hydrogen halide, or other small molecule from a benzene

derivative is a further route. The photodehydration of the 2-substituted phenol derivative **67**

leading to the benzoxetene intermediate **68**, which subsequently opens to the unstable *o*-quinone

methide **69**,[133,134] is one more example which tentatively can be attributed to alleviation of $S_1$

antiaromaticity of the benzene moiety (Scheme 15, reaction A). This reaction has found

applicability in organic synthesis because **69** obtained from **67**, and its derivatives with various

leaving groups (X = OH, Br, NMe$_2$, or SR with R being an alkyl), can readily be quenched by a

variety of nucleophiles.[135-138] It has further been reported that *o*-naphthoquinone methides (*o*-

NQMs) **71** and **74** can be formed upon irradiation of the hydroxy-naphthalenemethanols **70** and

**73**, respectively, at λ = 254 nm.[139] The quantum yields for reactions B and C of Scheme 15,

resulting in *o*-NQMs **71** and **74**, were determined to be Φ = 0.17 and Φ = 0.20, respectively. The

*o*-NQMs **71** and **74** were successfully trapped by Diels-Alder reactions with ethylvinylether leading to adducts **72** and **75**, respectively, with 87 % isolated yields in both cases. Through these results it is obvious that *o*-NQMs can be produced efficiently through photochemistry.
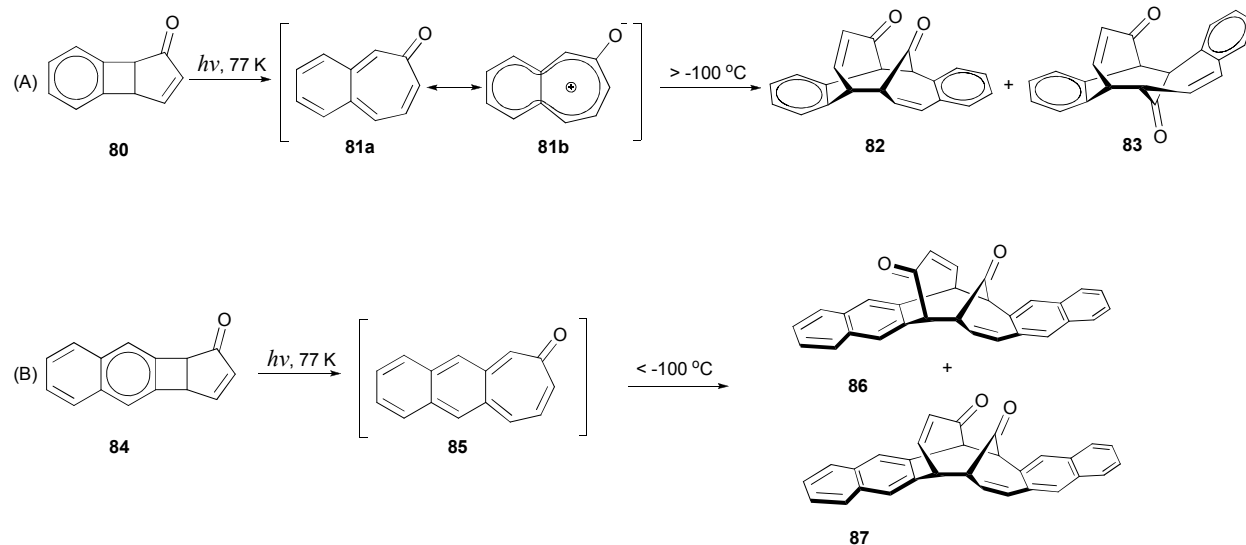


**Scheme 15**

More recently, Škalamera *et al.* showed that 3-hydroxymethyl-2-anthrol derivative **76** undergoes photodehydration leading to the *o*-quinone methide intermediate **77** upon its excitation to $S_1$ with light of $\lambda > 350$ nm.[140] The intermediate **75** decays to the trityl cation **78** upon protonation and the latter, after nucleophilic attack (Nu⁻ being a nucleophile such as MeO⁻, CF₃CH₂O⁻ or N₃⁻), can lead to a variety of products of type **79** (Scheme 16). Both **77** and **78** were detected through laser flash photolysis in deoxygenated TFE.
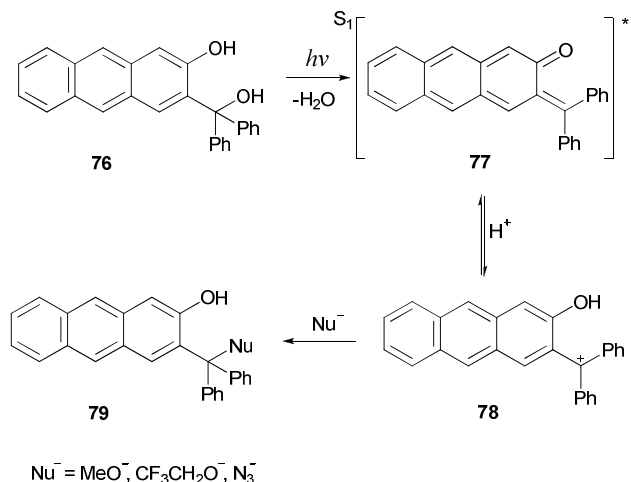
**Scheme 16**

Finally, Ohkita *et al.* observed the photochemical valence isomerization of the benzobicyclo[3.2.0]hepta-3,6-dien-2-one **80** when the latter was irradiated at 77 K in a 5:5:2 ether, isopentane, and ethanol (EPA) mixture with a high-pressure Hg lamp (Scheme 17, reaction A).[141] The observed photoinduced ring-opening was considered as exceptional because the non-benzannelated dienone did not undergo a similar photoreaction, indicating that the benzene ring and not the $\alpha,\beta$-unsaturated ketone segment is the chromophore. Moreover, the thermal reaction of **80** to **81** is demanding and does not proceed at temperatures below 200 $^{\circ}$C. This observation emphasizes the role of the ESAA character of the benzene ring in $S_1/T_1$ as a force to induce photorearrangements. Noteworthy, the conversion of **80** to **81** was practically quantitative. The *o*-quinodimethane intermediate was stable enough to be identified through infrared and UV-Vis spectroscopy at 77 K, but dimerization to **82** and **83** was observed at temperatures higher than -100 $^{\circ}$C. More recently, the same group reported that not only benzocyclobutene derivative **80** undergoes the photochemical ring-opening leading to *o*-quinoidal tropone intermediates but also naphtocyclobutene **84** when irradiated at $\lambda > 300$ nm (Scheme 17, reaction B).[142]
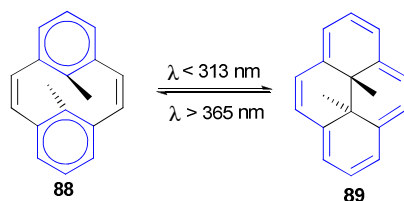
**Scheme 17**

## 6. The metacyclophanediene/dimethyldihydropyrene photoswitch and analogues

In this section we discuss [4$n$+2]annulenes that cannot undergo photorearrangements to $o$-xylylene derivatives as a way to break the excited state antiaromatic cycle. Such a case is the cyclophane **88**, containing two benzene rings (2 × 6π-electrons) which upon irradiation at λ < 313 nm (Scheme 18) can be photoswitched to its isomeric 15,16-dimethyldihydropyrene (**89**), a 14 π-electron annulene.[143-145] Simplistically viewed, the two benzene rings of **88** become reactive when photoexcited, leading to the formation of the isomer **89**. Yet, in the closed-ring isomer **89** the fourteen π-electrons are delocalized along the almost planar outer perimeter according to X-ray data obtained by Mitchell and coworkers.[146] The C-C bond lengths in this perimeter vary within the narrow range 1.389 – 1.397 Å, revealing that also **89** has Hückel-aromatic character in $S_0$ (1 x 14π-electrons). Similar to benzene such a system is expected to become antiaromatic in

its $T_1$ and $S_1$ state, and it should be prone to photochemical ESAA alleviation. Indeed, it undergoes photoinduced ring-opening which switches the compound back to **88** in a process that takes place upon irradiation with visible light ($\lambda > 365$ nm). Consequently, this switching between **88** and **89** is reversible and the system constitutes an important molecular switch. What makes this system particularly interesting is that both the **88** $\rightarrow$ **89** and **89** $\rightarrow$ **88** processes tentatively can be viewed as ESAA alleviations.[147]
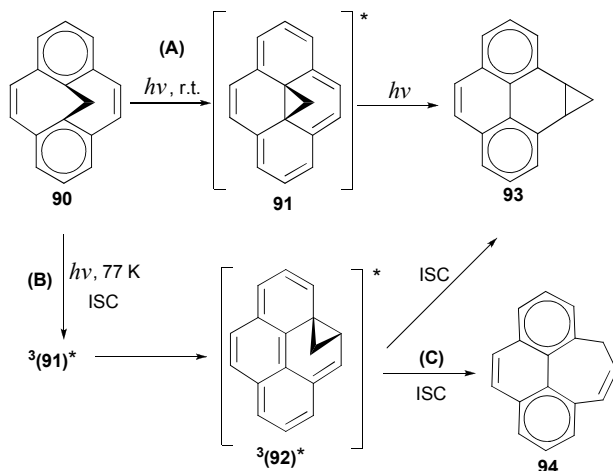


**Scheme 18**

Up until now, a large number of substituted as well as annelated analogues of the cyclophane **88** and its valence isomer **89** have been reported,[148] but the interpretation of the mechanism of both photoprocesses **88** $\rightarrow$ **89** and **89** $\rightarrow$ **88**, which is crucial for the evolution of this family of photochromic switches, has not been extensively studied. Robb and coworkers studied the mechanism of the photochromism of **88** using high-level CASSCF and CASPT2 calculations.[149] It was proposed that for the **88** $\rightarrow$ **89** (ring-closure) process, irradiation of **88** with UV light results in the formation of a singlet state biradical minimum which leads to its valence isomer **89** (more stable in the $S_0$ state than **88**) through internal conversion to $S_0$. According to this computational analysis this process is barrierless, which explains its high quantum yield. In terms of ESAA the biradicaloid excited state minimum, leading to the formation of the transannular bond, could correspond to a relief of ESAA. The reversed process **89** $\rightarrow$ **88** (ring-opening) is characterized by a synchronous flapping motion of the benzene rings, leading to the

transannular bond breaking and the alteration of the conjugation of the $\pi$-system. This flapping of the two former benzene rings, and therefore the avoidance of planarity of the $14\pi$-electron system of **89** in its excited state, could be considered as a mode for ESAA relief.

A compound with a similar photoreactivity is **90** reported by Wirz *et al.*.[150] This compound upon irradiation with a low-pressure Hg lamp ($\lambda_{max}$ = 254 nm) at ambient temperature undergoes an electrocyclic ring-closure in its $S_1$ state, resulting in the very unstable intermediate **91** (Scheme 19, photochemical route A).[151] According to Wirz *et al.*, **90** is initially excited to its $S_1$ state. As **90** contains two benzene rings (*i.e.*, $2 \times 6\pi$-electron systems), or in other words two Baird-antiaromatic rings, irradiation leads to the formation of the fluorescent intermediate **91**. Yet, **91** is a $14\pi$-electron system ($1 \times$ Baird-antiaromatic) which is unstable under the irradiation conditions and further photorearrangement leads irreversibly to dihydro-9H-cyclopropa[e]pyrene (**93**) as the final product.

Through triplet sensitization provided by benzophenone Wirz *et al.* in addition detected another intermediate, derivative **92** in its $T_1$ state, when photolysing **90** in an EPA glass at 77 K (Scheme 19, route B).[148] Its formation was attributed to the photoisomerization of **91**. This intermediate either leads to the final product (mutual for routes A and B of Scheme 19) or intersystem crosses to its $S_0$ state leading to another isolated product: compound **94** (Scheme 19, reaction C). Route B can also be interpreted in terms of excited state antiaromaticity of the two benzene rings of **90** as formation of the non-aromatic compound **92** upon irradiation of **90** is a way for this system to avoid antiaromaticity in its $T_1$ state.

**Scheme 19**

## 7. Photodissociation of halobenzenes

As described above, benzene has a first excitation energy which is significantly higher than that of the isomeric pentafulvene (4.90 *vs.* 3.45 eV, respectively)[75,76]. Thus, substituted benzenes where the bond strengths to the substituents X are relatively weak will be prone to photodissociation if there are couplings between the lowest $\pi\pi^*$ state and states which are C-X dissociative. The most apparent such systems are halobenzenes for which the C-X bond strength is lowered gradually as one descends Group 17 with homolytic bond dissociation energies going from 5.1 eV for the C-F to 2.9 eV for the C-I bond.[152,153] For dissociation the $\sigma^*$ orbital should be populated and in the halobenzenes there are two types of dissociative states; the $\pi\sigma^*$ and the $n\sigma^*$ states. According to computations the first $\pi\sigma^*$ states are of lower energy than the $n\sigma^*$ states, both for the states of singlet and triplet multiplicities. As the $S_1$ state, which is of $\pi\pi^*$ character, is located at similar energies in the various monohaloalkanes (235 - 275 nm)[154] and in benzene, the crossing point between the $S_1$ state, which is C-X bonding, and the $\pi\sigma^*$ dissociative

states will gradually move to lower energies as one descends Group 17. Indeed, one may

conclude that it is the antiaromatic character of the $S_1$ state, pushing the state to higher energies,

which is the very cause of the photoinstability of heavier arylhalides. In 4-bromofluorobenzene

the energies of the various states of singlet as well as triplet multiplicity vary qualitatively with

C-Br distance as shown in Figure 9, which is based on the CASPT2//CASSCF calculated
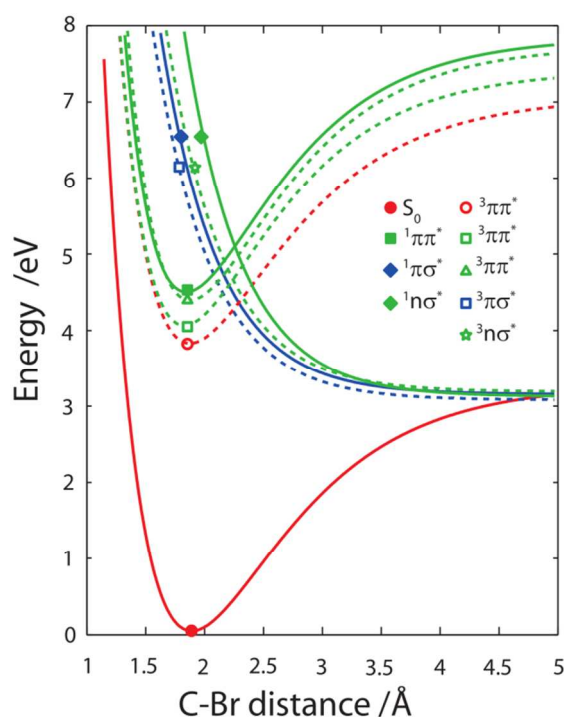
potential energy curves of this molecule.[155]



**Figure 9**: Schematic drawing of the diabatic potential energy curves of the five lowest bound

and the four lowest C-Br repulsive states of 4-bromofluorobenzene from ref. 156. The drawing is

based on CASPT2//CASSCF energies reported in ref. 155. Copyright Daniel Karlsson 2008.

The competition between photophysics and photochemistry becomes clear as the crossing point

between the bound $S_1$ state and the dissociative $\pi\sigma^*$ states moves down in energy as one goes

from fluoro- (**95**), to chloro- (**96**), to bromo- (**97**), and iodobenzene (**98**). Photolysis of **95**, even at 193 nm, does not lead to C-F bond scission but elimination of HF and C-H bond cleavage is instead observed.[157,158] Chlorobenzene, on the other hand, when irradiated at 254 nm in the vapour phase displays a quantum yield for photolysis of 0.4.[159] The quantum yield for dissociation of bromobenzene has not been reported but the emission quantum yield in solution is lower than that of chlorobenzene,[160] implying that the photodissociation quantum yield is higher than 0.4. For iodobenzene the repulsive state is reached directly upon excitation at 266 nm giving a quantum yield for photolysis close to unity.[161-163] The lifetime in the $S_1$ state also varies, with the longest for chlorobenzene (1 ns) and the shortest for iodobenzene (0.7 ps).[161,163,164] For the bromo- and iodobenzene there is a coupling of the $\pi\pi^*$ $S_1$ state with a dissociative $^3\pi\sigma^*$ state, *i.e.*, it involves an intersystem crossing to a triplet state.[161,165-167] However, the dissociation of chlorobenzene has been concluded to be more complex with two dissociation channels with a slow dissociation channel represented by a hot molecule mechanism and a faster dissociation channel interpreted as a coupling of the $\pi\pi^*$ $S_1$ state with a dissociative $^1\pi\sigma^*$ state.[168,169] Consequently, the photodissociation of the carbon-halogen bond in arylhalides is a route for ESAA alleviation through the coupling of the antiaromatic $\pi\pi^*$ $S_1$ state with a dissociative $\pi\sigma^*$ state, either of singlet (X = Cl) or triplet (X = Br or I) multiplicity. From this one may postulate that arylhalides should have a higher photostability provided that there are additional better channels for ESAA alleviation. This might be the case in 4-halostyrenes where rotation about the olefin C=C bond could provide for such alleviation.

## 8. Photochemical reactivity of two selected heteroaromatic compounds

The excited state antiaromaticity concept could also be extended to hetereoaromatic compounds which have $\pi\pi^*$ states instead of $n\pi^*$ states as their lowest excited states. The obvious selection are heteroaromatics without $\sigma$-type lone pairs ($n_\sigma$) as these compounds only will have $\pi\pi^*$ states, similar to benzene. Here we discuss pyrrole (**99**) where the lone-pair of the tricoordinate N atom is of $\pi$-type ($n_\pi$) and involve in the $6\pi$-electron cycle, and silabenzene (**100**) where one C atom in benzene is replaced by an isovalent sp$^2$ hybridized Si atom. Still, excited state antiaromaticity can possibly also be expanded to heteroaromatics with $n_\sigma$ lone-pairs provided that the first $\pi\pi^*$ transition has been pushed to lower energies than the $n\pi^*$ transition. This is the situation in pentafluoropyridine when compared to pyridine.[170] Yet, heteroaromatic molecules, despite that their lowest transitions are of $\pi\pi^*$ character, may repolarize the electron density as a way to avoid the ESAA. This feature which is not accessible for benzene could lead to a photochemistry which is different from that of benzene.

The photochemistry of pyrroles has only been studied sparsely. It has been shown that several pyrrole derivatives undergo certain photorearrangements which are considered to be their most characteristic photoreactions.[171] As Barton and Hussmann reported about thirty years ago, mono- and *bis*(trimethylsilyl)pyrroles **101** undergo photorearrangements when exposed to UV-light (Scheme 20).[172] In case of the monosilylated derivative (R = H) its irradiation with UV-light, using a medium-pressure Hg lamp results in product **102** in high conversion (84 %), whereas in case of the *bis*(TMS) derivative, irradiation led to a mixture of the isomeric products **103** and **104** in high overall conversion. These reactions are thought to proceed *via* electrocyclic ring-closure to a 5-azabicyclo[2.1.0]pentene **107a**, with subsequent [1,3] N-shift leading to the intermediate **107b**, and finally ring-opening leading to the product **108** (Scheme 21).

Noteworthy, the intermediates **107** correspond to Dewar-pyrrole, and access to these products is facilitated with substituents that stabilize the polarized excited state **106** where the polarization could be viewed as a way for ESAA alleviation. This polarization triggers the photorearrangement to **108**, and similar photorearrangements have been reported for cyano substituted pyrroles.[173,174]
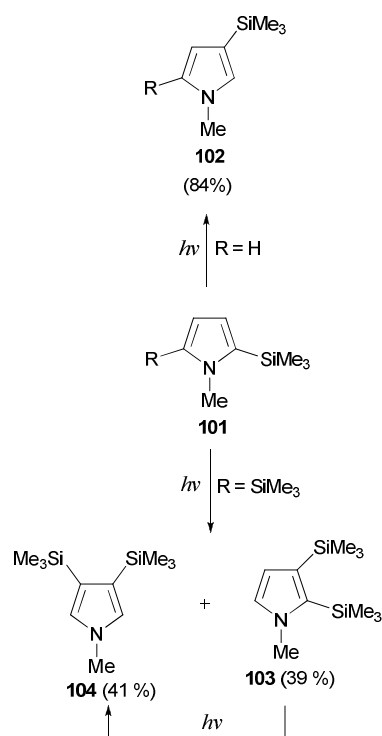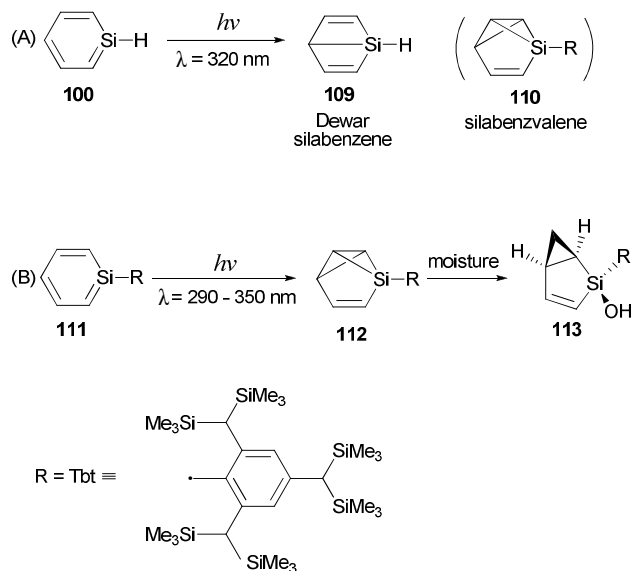


**Scheme 20**
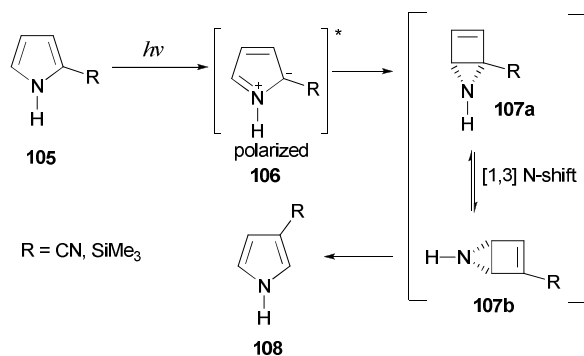
**Scheme 21**

Silabenzene (**100**) is an $S_0$ state aromatic, yet, highly reactive benzene analogue which has

attracted interest from both synthetic and theoretical chemists.[175-177] It is valence isoelectronic to

benzene and its photochemistry has been examined at cryogenic temperatures through the matrix

isolation technique.[178] More recent and deepened contributions on the photochemistry of

silabenzenes were, however, provided by Tokitoh and co-workers who synthesized and

crystallographically characterized the kinetically stable silabenzene **111**, and also investigated its

room-temperature photochemistry.[179] Even though the photolysis study of the parent silabenzene

**100** in a cryogenic Ar matrix at $\lambda$ = 320 nm by Maier *et al.* resulted in some evidence for

formation of Dewar silabenzene **109** (Scheme 22, reaction A),[178] the photolysis of **111**

unambiguously gave silabenzvalene **112** in an approximate 80% yield (Scheme 22, reaction B).

This compound was moisture sensitive and only the silanol **113** was isolated. Still, the formation

of **112** was confirmed through ^{1}H and ^{13}C NMR techniques. In contrast, the previously alleged

formation of Dewar-silabenzene **109** through photoreaction A of Scheme 22 was only based on

shifts in the Si-H stretching frequency observed upon irradiation of **100**. Further support for the

formation of silabenzvalene in photolysis of silabenzenes came through the recent computational

study on the photochemistry of **100** by Su.[180] He showed that the formation of silabenzvalene **110** is kinetically favored when compared to formation of isomeric silabenzvalenes as well as of Dewar-silabenzene **109**.



**Scheme 22**

## 9. Photocycloaddition reactions of benzene

Except for the photoaddition reactions between styrenes and alcohols we have up until now discussed unimolecular reactions of benzene and various benzene derivatives. Yet, benzene in its $S_1$ antiaromatic state also participates in bimolecular photoreactions, and in this final section we discuss photocycloaddition reactions with alkenes.

Benzene derivatives are prone to a number of interesting photoreactions which in many cases are important for synthetic chemistry as they lead to products difficult to synthesize with other than

photochemical means exactly because of the aromatic stabilization of benzene in its $S_0$ state. The photocycloadditions of alkenes to benzene and its derivatives are important such examples. The latter photoreactions were developed independently by Wilzbach and Kaplan,[181] and Bryce-Smith, Gilbert and Orger,[182] almost 50 years ago, and they have been extensively described in a number of review articles.[183-186] There are three different types of alkene photocycloadditions to benzene, namely the [2+2] or *ortho*, the [2+3] or *meta*, and the [2+4] or *para* photocycloadditions (Scheme 23). A common feature for most of these photoreactions is that they proceed *via* pathways initiated with benzene in its antiaromatic $S_1$ state.[187] As seen above, this antiaromatic state is highly reactive, resembling cyclobutadiene in its $S_0$ state, and the photocycloadditions with alkenes lead to either of adducts **115 - 117**.
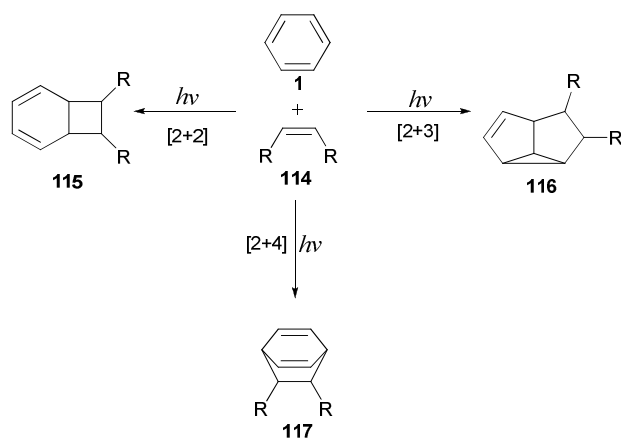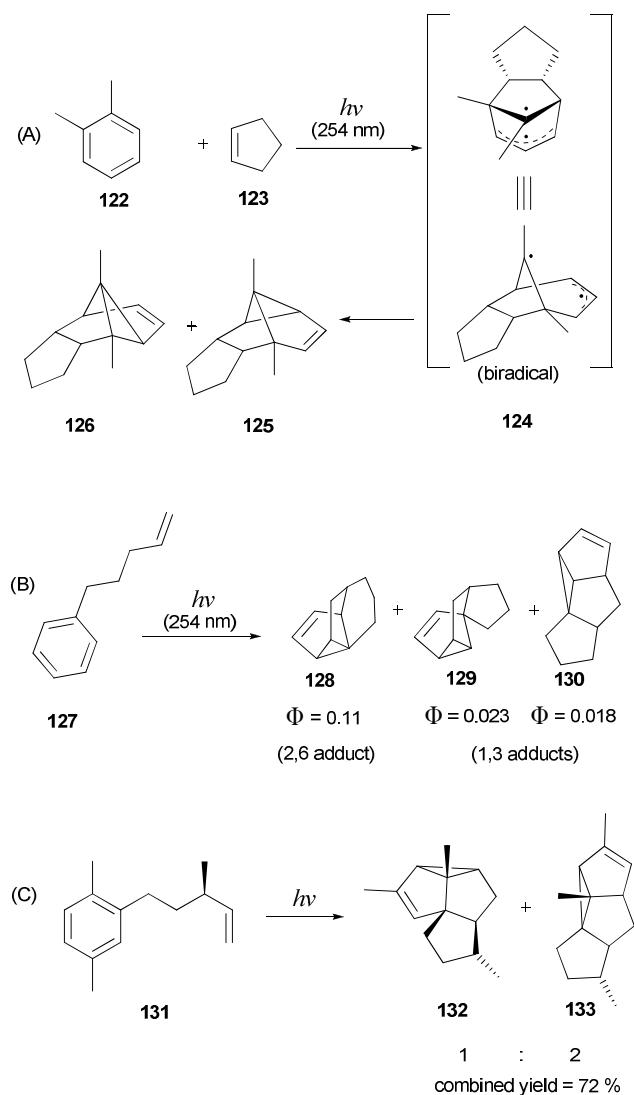


**Scheme 23**

Interestingly, the mechanism involves the formation of an exciplex (**118**) of benzene in $S_1$ and the alkene in its $S_0$ state, as shown for the [2+3] photocycloaddition of ethylene to benzene in Scheme 24.[188,189] This exciplex subsequently leads to formation of a biradical (**120**), which finally yields adduct **121**.
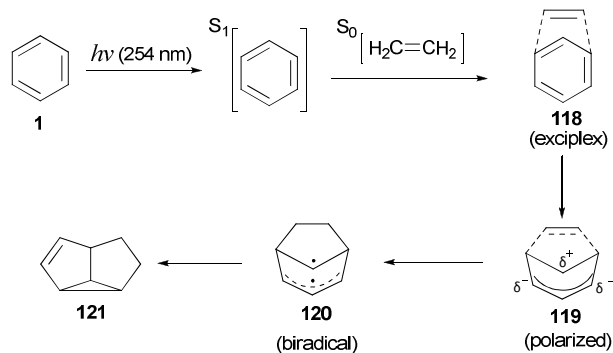
**Scheme 24**

An interesting example is the synthesis of compounds **125** and **126** as photoaddition adducts between cyclopentene (**123**) and *o*-xylene (**122**), reported by Reedich and Sheridan (Scheme 25, reaction A).[190] Evidence of the biradical intermediate **124**, produced upon excitation of *o*-xylene ($\lambda = 254$ nm) and subsequent reaction with the alkene **123**, was also provided. What is interesting is the high complexity gained in a single photochemical step starting with very simple reactants. The high photoreactivity of benzene and its derivatives in $S_1$ against alkenes has been exploited extensively in synthetic organic chemistry. In cases where the intramolecular photocycloaddition of an alkene group to a benzene derivative are possible such photoreactions can lead to adducts of significantly high complexity, as for instance in the case of 5-phenyl-pent-l-ene (**127**).[191] In a similar way to the intermolecular reaction A of Scheme 25, excitation of the benzene ring of **127** at $\lambda = 254$ nm triggers the photoaddition of the alkene end group. The adducts **128–130** are formed with **128** (the 2,6-adduct) as the main product in a process with a quantum yield $\Phi = 0.11$ (Scheme 25, reaction B).

**Scheme 25**

A *p*-xylene based analogue of **127**, compound **131**, shows a similar photoreactivity and results in

the formation of adducts **132** and **133** at high yield (72 % combined), as reported by Wender and

Singh (Scheme 25, reaction C).[192] This reaction provided access to the tetracyclic adduct **132**

which is a precursor of (-)-retigeranic acid. The latter example on formation of a highly complex

molecule shows the immense potentials of the photoreactivity of benzene in its antiaromatic $S_1$

state. Recently, it has also been shown that similar photocycloadditions are possible for pyrroles

leading to molecules with notably high complexity.[193] Clearly, these photoreactions can serve as important tools in synthetic chemistry, especially in the construction of complex natural products.


## Conclusions and Outlook

The benzene ring forms part of chromophores in a range of different compound classes which in response to irradiation undergo various photochemical reactions. A broad knowledge on these reactions has been gathered within experimental organic photochemistry. On the other hand, within the theoretical and computational chemistry community there has been a gradually growing interest in aromaticity and antiaromaticity effects in the lowest $\pi\pi^*$ excited states of simple annulenes. It should be time to put these two areas in connection as it likely could foster development of new photochemistry as well as provide deepened mechanistic understanding of established photoreactions.

The field emerged in 1972 when Baird used perturbation molecular orbital theory to investigate the (anti)aromaticity of structures that correspond to minima in the lowest $\pi\pi^*$ triplet states of annulenes.[1] He concluded that the electron counts for aromaticity and antiaromaticity are reversed in the triplet state as compared to what is the case for the closed-shell singlet state, given by Hückel's rule. Thus, benzene in its $T_1$ ($1^3B_{1u}$) state is antiaromatic and destabilized relative to a species with linear instead of cyclic $\pi$-conjugation. Much more recently, it has been found based on quantum chemical calculations that Baird's rule can be extended to the first singlet excited state, which means that the $S_1$ ($1^1B_{2u}$) state of benzene is antiaromatic.[5]

Herein, we reviewed the earlier theoretical and computational contributions on the antiaromaticity of benzene in its $T_1$ and $S_1$ states, and thereafter, describe a range of photochemical reactions of benzene derivatives that can be viewed as a drive of the benzene ring to alleviate its excited state antiaromaticity (ESAA), as schematically shown in Figure 1. We argue that with the finding that the benzene ring is antiaromatic in $T_1$ and $S_1$, combined with the plethora of photoreactions in which the excited benzene ring in a molecular framework reshuffles its structural neighborhood, should motivate the notation of the benzene ring as a molecular "Dr. Jekyll and Mr. Hyde". Though, in contrast to the fictitious Mr. Hyde it is under illumination (not during the dark hours) that benzene reveals its unknown and evil "Mr. Hyde" character. In our view the recognition of the "Jekyll and Hyde" character of benzene has great potential to open new vistas for organic photochemistry and many related areas in which compounds and materials with benzene rings are exposed to light.

The different benzene photoreactions on which the concept of ESAA alleviation can provide for qualitative rationalizations is likely not limited to the series of photoreactions considered herein. For example, photosubstitution reactions of aromatic compounds are in most cases considered to progress *via* the $\pi\pi^*$ excited triplet state, although some reactions start with $\pi\pi^*$ excited single state.[194] Regardless if in the $\pi\pi^*$ triplet or singlet state these would all be strongly influenced by the ESAA of the benzene ring in these states.   Another interesting reaction is the photocyclization of benzannelated enediynes.[195-197] These species upon excitation to their lowest $\pi\pi^*$ singlet excited state (influenced by ESAA) tend to accept an electron, leading to radical-anion intermediates that undergo intramolecular ring closures. The electron transfer to the excited benzannelated enediyne could tentatively be viewed as a way for ESAA alleviation. Such photoreactions have found applications in DNA photocleavage.[198,199] Photochemical aromatic

substitution reactions and photocyclizations of benzannelated enediynes are just two additional examples and there are likely many other photoreactions that could be viewed as reactions leading away from an excited state antiaromatic benzene ring. In conclusion, it is time to recognize that the benzene ring has a dual character and to exploit this in various applications, in particular to exploit its hitherto unrecognized molecular "Mr. Hyde" character.

## Acknowledgements

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