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9-Aryl-Phenalenones: Bioinspired Thermally Reversible Photochromic Compounds for Photoswitching Applications in the Pico- to Milliseconds Range

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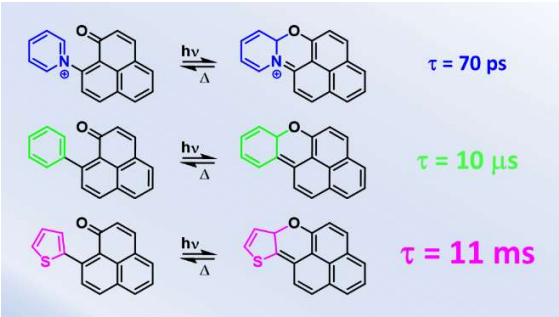
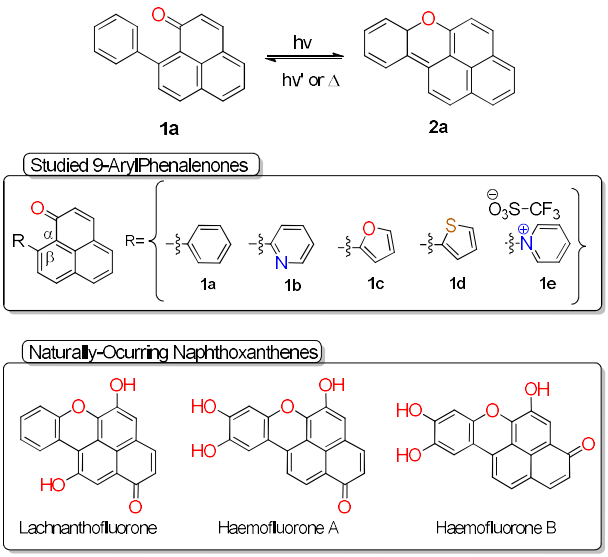
Supporting Information Placeholder



ABSTRACT: Ultrafast photochromic molecules are being actively investigated to meet the demand of fast optical switching systems. Inspired on the irreversible cyclization of 9-phenylphenalenone plant metabolites to yield highly-coloured naphthoxanthenes for defense purposes, aryl-substituted phenalenones have been developed that undergo a similar but reversible photochromic reaction. The lifetime of the naphthoxanthene photoisomer spans nine orders of magnitude, ranging from tens of picoseconds to tens of milliseconds depending on the electronic properties of the 9-aryl group.

Nature has evolved a rich repertoire of materials and systems that can reversibly adjust their structure and properties in response to environmental stimuli.[1] Light as a stimulus presents the advantages of high spatio-temporal control as well as insensitivity to environmental factors, and can be applied in an external, non-invasive, and residue-free fashion.[2] Molecules with photochemically switchable properties play a crucial role in a wide range of modern applications, including functional molecules, their assemblies, materials used for data storage and logic operations in optoelectronic devices, as well as biotechnological and pharmacological applications, especially for optogenetics and imaging.[3-7] Thus, photochromic compounds capable of reversibly photoisomerizing between at least two different (meta)-stable isomers with markedly different properties, e.g., geometry, spectroscopic signature, polarity, magnetic state, spatial ordering or surface tension,[8-12] are the subject of current interest for fast optical switching applications.[13] T-type photoswitches, where the photochemically-generated isomers revert thermally to the initial form, are of advantage for some applications because no additional photons are needed to bring the system back to its original state.[14-17]

Scheme 1. Top: Reversible ring closure and opening in 9-phenyl-phenalenone.[18,19] Middle: Structure of the 9-arylphenalenones studied in this work. Bottom: Naturally-occurring naphthoxanthenes derived from 9PPNs.



Previous work from our laboratories has revealed that 9-phenylphenalenones (9PPNs) can undergo reversible photocyclization upon light excitation, a process termed β-phenyl quenching (BPQ).[18-20] The closed-ring structure, a naphthoxanthene (NX), is unstable due to the loss of aromaticity and spontaneously reverts to the starting material (Scheme 1 top). Photocyclization of 9PPNs is at the heart of a mechanism used by plants to defend themselves from pathogens.[21-24] 9PPNs produce reactive oxygen species when exposed to UV and blue light[25-28] and produce secondary metabolites capable of absorbing light at longer wavelengths (Scheme 1 bottom).[29-33] The structural similarity between these metabolites and the NXs produced in the cyclization of 9PPNS, suggests a common mechanism of production. A major difference is the superior stability of the natural counterparts conferred by rearomatization of the NX form by hydroxy-oxo tautomerization. In the course of our investigations on bioinspired phenalenone derivatives,[34,35] we discovered that it is possible to alter the stability of the closed NX form by modifying the substituents in the 9-phenyl group. In this work we show that replacing the phenyl substituent by heteroaryl groups (Scheme 1 middle) results in a dramatic variation of the NX lifetime over nine orders of magnitude.

All the 9-arylphenalenones **1a-1e** absorb in the ultraviolet and blue regions with a tail that extends to 500 nm (Figure 1, panels A-E). Nanosecond laser flash photolysis of **1a-1d** in argon-saturated solutions produced long-lived transients (Figure 1, panels F-I), which were assigned to the corresponding NXs **2a-2d** following the protocols of our previous work.[19,36] **1e** showed a different behavior and is described separately below. The kinetics of NX production in **1a-1d** were biphasic (Figure 1, panels K-N), showing a fast-initial spike and a slower rise, which indicate that the NXs are formed from both their singlet and triplet states. Consistent with this, the triplet lifetimes, deduced from the slow-rise component, were more than one order of magnitude shorter than that of the unsubstituted PN, which cannot undergo photocyclization (Table S1). Moreover, the slow rise component disappeared upon aeration (Figure 1, panels K-N) and singlet oxygen production was observed (Table S1 and Figure S1), indicating efficient oxygen quenching of the triplet state. The decay of the NX form was insensitive to oxygen but its lifetime was strongly affected by the nature of the arylic substitution at position C-9, increasing from a few microseconds for **2a**,**b** to tens of milliseconds for **2c**,**2d**. The trend is in concordance with the measured activation energy for ring opening (Table S1 and Figure S2). Of note, **2d** (panel S) showed a spectral evolution over the course of its decay, indicating further structural changes after initial production of the NX form (see below).

Strikingly different observations could be made for **1e** (Figure 1, panels J,O,T). The transient showed a very fast decay component (70 ps ~ 14 GHz) as probed by femtosecond transient absorption) and a longer-lived component decaying in the microsecond time scale. The spectrum of the early transient is very similar to that of the NXs **2a-2d** and is tentatively assigned to the NX form **2e**. The longer-lived component shows a spectrum similar to that of triplet PN[37,38] and could be quenched by oxygen to produce singlet oxygen, indicating that it corresponds to the triplet state (Table S1 and Figure S1). Thus, it would seem that, for this particular compound, the NX form **2e** would be formed only from the singlet state.

Theoretical calculations provide support and further insights for the above observations. The excited-state pathway for ring closure in **1a** is the addition of the ketone moiety to the *ortho*-position of the 9-phenyl-ring (**2a**), whereas *ipso*-addition suffers from endothermicity and a concomitant higher barrier, as reported previously.[19] For the 2-pyridyl derivative **1b**, a novel situation arises in that the aromatic substituent on the phenalenone system no longer has a plane of symmetry. In principle, *ortho*-addition can take place to two sides of the pyridine ring, and there are two rotamers of the ketone (red and grey lines in Figure 2). The calculations show that addition to the 3-position of the pyridine ring (**2b**) should be the preferred site of attack. *Ipso*-addition (**2b'**) is predicted to be hindered by a large barrier, which is unsurprising, as this position is very electron-poor. Addition to the pyridine N (**2b"**; red line in Figure 2) is predicted to have a fairly small barrier. However, this reaction pathway is both endothermic and endergonic, and therefore unlikely to be of any significance. What is remarkable about this system is the fact that **2b"** appears to have a triplet ground state, which may be due to some degree of antiaromaticity, as the middle top ring has eight π-electrons. This antiaromaticity is probably also reflected in the fairly high barrier calculated for the ring-opening of singlet **2b"**. The kinetics of ring-opening of **2b** is predicted to be similar to that of **2a** (black line in Figure 2). For the *ipso*-addition, there is only one TS, in which the two ring systems are perpendicular to each other. Coming from the *ipso*-biradical, the system therefore will have to pass a valley-ridge-inflection point to bifurcate to either the *syn*- or *anti*-conformer of the ketone triplet. This also holds for the other heterocyclic systems.

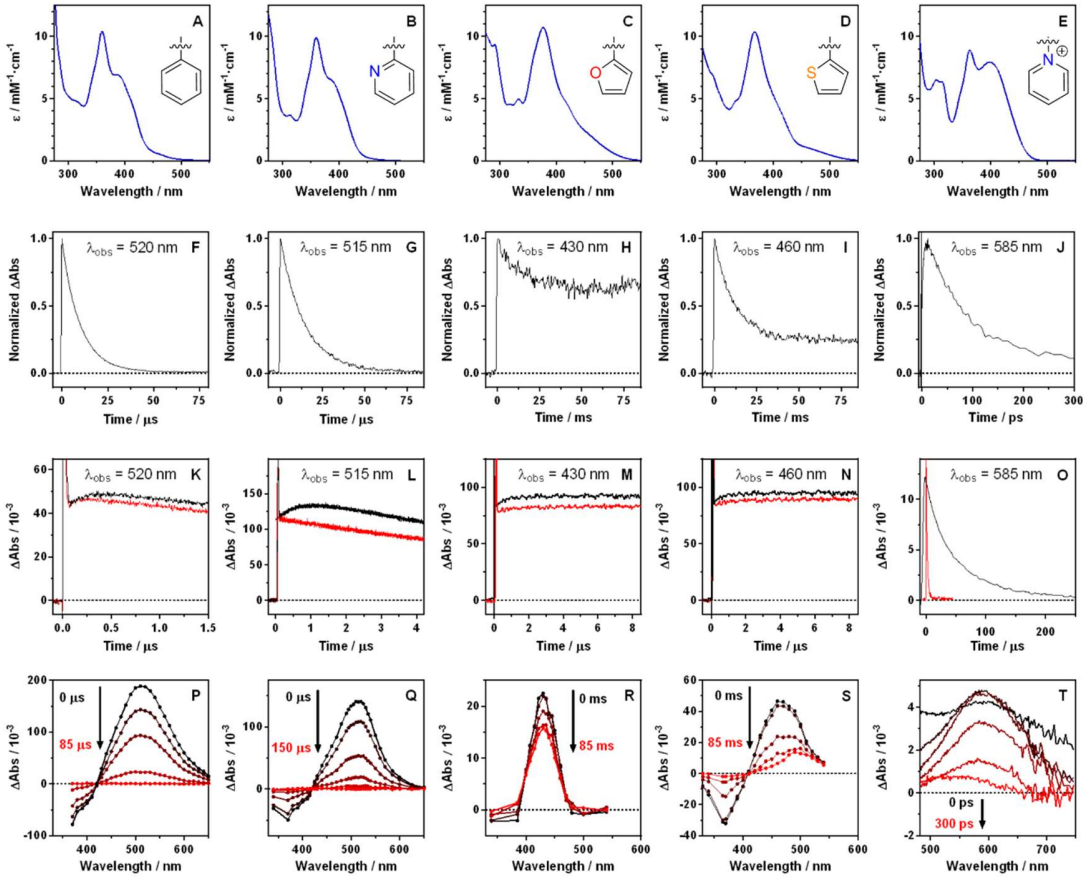


Figure 1. Photophysical characterization of **1a** (A,F,K,P), **1b** (B,G,L,Q), **1c** (C,H,M,R), **1d** (D,I,N,S) in acetonitrile and **1e** (E,J,O,T) in PBS (pH 7.4); λ_{exc} = 355 nm. (A-E): Absorption spectra. (F-J): **2a-2e** Transient absorption traces in argon-saturated solvent (black line). (K-O): Microsecond transient absorption traces under argon (black line) and air (red line). (P-T): Transient absorption spectra at different timescales.

In the case of the 2-substituted 5-membered heterocycles, again the presence of two different rotamers of the ketones has to be considered (Figure S3). However, addition can only take place to one side, as addition to the heteroatom appears to be an unlikely option. The barrier for ring-opening of **2c** and **2d** is predicted to be on the order of 18 kcal mol^{-1}, which is significantly higher than that of **2a-b**, resulting in millisecond range lifetimes for **2c,d**. Unlike the phenyl- and pyridyl-substituted derivatives, *ipso*-addition is predicted to be considerably faster than *ortho*-addition for **1c**, while it should be similarly fast for **1d**. To our delight, the transient absorption results are consistent with these predictions (Figure 1 panels H,I): the transient initially assigned to **2c,d** contains in fact two components, which, in the light of the calculations, we assign to the transient *ortho*-adducts (**2c,d**, shorter lived) and products (**3c**, **3d**, lifetime in excess of 100 ms) derived from *ipso*-(**2c',d'**) adducts. Thus, the *ipso*-pathway is favoured in the furyl derivative (larger amplitude) but the *ortho*- in the thienyl one (smaller amplitude). Calculated UV/Vis spectra corroborate the assignment of the residual absorption observed upon LFP of **1c** and **1d** to aldehyde **3c** and thioaldehyde **3d**, with excellent agreement between the residual absorption in Figure 1R / 1S and the calculated spectra of **3c** / **3d** (see Figures S6 and S7, SI).

Ipso-addition has been previously observed for triplet β-phenylpropiophenone, where it is the main decay pathway.[36,39-43] The intermediate biradical formed in this system is very short-lived (< 20 ps) and deactivates back to the starting material. The results of our experiments and calculations indicate a possible different outcome for the corresponding biradicals **2c'** and **2d'**. Specifically, formation of stable photoproducts, e.g. **3c**, can be expected for these molecules (Figure 2), which is consistent with the trend in photostability **1c** < **1d** << **1b** < **1a** (Figure S4).

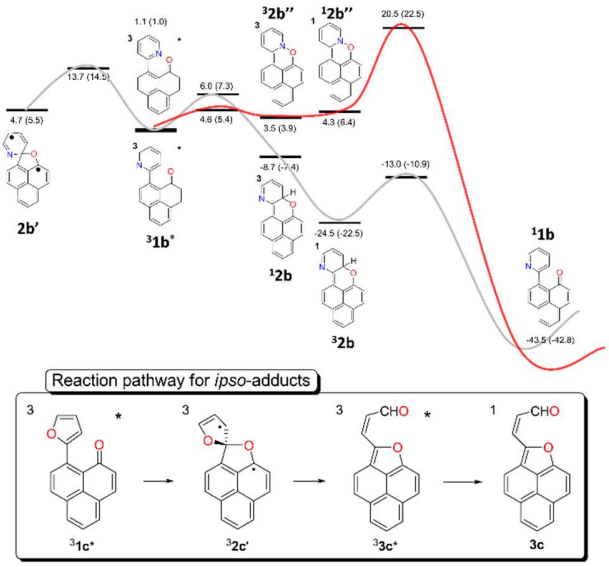


Figure 2. Top: Reaction pathways after triplet excitation of **1b**. Energies (without brackets) and Gibbs free energy (brackets), as calculated at the ((U)M05-2X/cc-pVTZ) level of theory, are given in kcal/mol relative to the triplet state. Solid lines connecting the different states are provided as a visual aid only. Bottom: Pathways of ipso-adduct decay in **2c**.

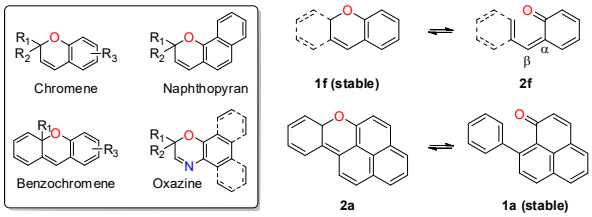
Formation of **3c** from ^{3}**1c*** is exergonic by ΔG = -33.6 kcal mol^{-1}, but should be slow because the calculated free energy of activation for ring opening of ^{3}**2c'** to ^{3}**3c*** is quite significant in the gas phase ($\Delta G^{\ddagger}$ = 19.5 kcal mol^{-1}). However, a surface-crossing mechanism, yielding ground-state **3c** directly from ^{3}**2c'** might explain the formation of **3c.** Or **3c** is directly formed from **1c** on the singlet excited state surface. Attempts to isolate the photoproducts failed but we have obtained a compound very similar to **3c** from the reaction of 9-trifluoromethanesulfonyloxy-phenalenone with sodium azide.[44]

Striking differences set the derivative **1e** apart from **1a-1d**: Transient absorption experiments (Figure 1, panels J,O,T) indicate that **2e** is produced only from the singlet excited state, while the triplet state yields exclusively singlet oxygen. Consistent with these observations, theoretical calculations indicate that **2e** production from the triplet state is unlikely due to a very high activation energy (Figure S5). On the other hand, the barrier for electrocyclic ring opening of **2e** is calculated to be 4-5 kcal mol^{-1}, significantly smaller than for **1a** (ca. 10 kcal mol^{-1}), which is consistent with the 70 ps lifetime observed for **2e**. Such ultrafast (~ 14 GHz) oscillation rate is ideal for high-end optical switching applications.

The significance of the results can be gauged in the light of the biological role of 9-phenylphenalenones, which participate in plant defense against pathogen infections, either directly or through the production of coloured naphthoxanthene secondary metabolites.[21-33] The study of such process led us to the discovery of a thermally-reversible photocyclization reaction to produce metastable naphthoxanthenes.[18-20] The current work demonstrates that this reversible photochromism can be extended to phenalenones substituted with heteroaryl moieties such as pyridyl, furyl, thienyl and pyridinium. The loss of local aromaticity in the closed forms is the driving force for the ring opening reaction. Thus, by modulating the electronic nature of the aryl group at position C-9, it is possible to fine-tune the lifetime of the closed-ring isomer over nine orders of magnitude, from tens of picoseconds to tens of milliseconds. The theoretical insights gained suggest that further widening of this time span is possible.

It is interesting to note that the photocyclization and subsequent thermal ring opening in 9-aryl-phenalenones share many similarities with the photoisomerization process of chromenes (e.g., naphthopyrans, benzo[b]chromenes or oxazines among others; Scheme 2) but, surprisingly, the process occurs in the opposite direction.[45-48] The stable isomer in chromenes is the closed form (**1f**), which undergoes ring opening to the less stable α,β,γ,δ-unsaturated ketone (**2f**) upon photoirradiation. Close inspection of the structure of **2f** reveals that the reverse reaction is a cycloaddition between the carbonyl and the newly-formed vinyl group in the β-position, which is very similar to the photocyclization reaction in 9-aryl-phenalenones.

Scheme 2: Left: Representative structures of the different families of chromenes. Right: Reaction pathway for 2H-chromene core (1f) and 9-phenylphenalenone (1a).



It can therefore be postulated that 9-aryl-phenalenones can be considered as "inverted-chromenes", in which the open form is more stable because the local aromaticity of the phenalenone and of the aryl substituent is preserved. In contrast, it is the closed structure of chromenes that preserves the aromaticity of the system,[45,49] even when it contains vinyl- or aryl- β-substituents.[50] Interestingly, the open form of 12a*H*-12a-methylnaphtho[3,2]chromene has been reported to undergo a photocycloaddition reaction yielding the *ipso* adduct.[51,52]

In summary, photoexcitation of a series of bioinspired 9-arylphenalenones (**1a-1e**) leads to the formation of their corresponding naphthoxanthenes (**2a-2e**), which thermally revert to the original 9-arylphenalenones (**1a-1e**) with time constants ranging from ultrafast (picoseconds) to milliseconds depending on the electronic density of the aryl substituent. The results obtained provide a sound basis for the development of 9-aryl-phenalenones as a new family of thermally reversible photochromic compounds. Of specific interest, compound **1e**, with an oscillation

frequency ~ 14 GHz, shows strong promise for ultrafast photoswitching applications.

ASSOCIATED CONTENT

Supporting Information

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

Experimental procedures (materials, general spectroscopic measurements, computational methods). Singlet oxygen quantum yield determination for **1a-1e**. Arrhenius plots for **2a-2d**. Calculated photoreaction pathways for **1c-1e**. Photostability studies for **1a-1d**. (PDF)

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Author Contributions

All authors discussed on the results and commented on the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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