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Anion- π interactions in light-induced reactions. Their role in the amidation of (hetero)aromatic systems with activated N-aryloxyamides

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Abstract: The importance of anion- π interactions as a driving force for chemical and biological processes is increasingly recognized. In this communication, we describe for the first time its key participation in light-induced reactions. We show, in particular, how transient complexes formed through non-covalent anion- π interactions between electron-poor *N*-aryloxyamides and multiply charged anions (like carbonate or phosphate) can experience facile light-promoted N-O cleavage, affording amidyl radicals that be subsequently trapped by (hetero)aromatics.

The contemporary development of light-promoted reactions has mostly relied on the use of different types of photocatalysts, such as metal complexes,^[1] organic dyes^[2] and semiconductors.^[3] However, the presence of a photocatalyst in light-mediated processes is not always required. One common catalyst-free activation mode involves the formation of charge-transfer (CT) complexes, with electron donor-acceptor (EDA) complexes as the best known example^[4] whose relevance in organic synthesis has been documented by a plethora of reports.^[5] These CT complexes can arise from different non-covalent interaction modes,^[6] as for instance hydrogen bonds^{[7]} and $\pi\text{-}\pi$ interactions. $^{[8]}$ Anion- π complexes, in turn, are transient species resulting from interactions^[9] between electron-poor aromatic systems^[10] and anions. First described in 2002,^[11] their unexpected stability^[12] has been proven to derive from a combination of electrostatics and polarization induced by the anion. In spite of the importance they have in supramolecular chemistry^[13] as well as in biological processes,^[14] the role of anion- π interactions in (photo)catalysis remains largely unexplored.^{[15],[16]} In the last years, Leonori and coworkers have reported how hydroxylamine derivatives work efficiently as nitrogen-centered radical precursors^[17] in photochemical transformations,^[18] which are mediated either by different kinds of photocatalyst or by the formation of EDA complexes,^[19] sometimes in the presence of inorganic base (K₂CO₃).^[20] Since multiply charged anions, like carbonate, are privileged actors in anion-π interactions, we wondered whether an anion- π interaction might enable the light-mediated formation of amidyl radicals. Conceptuality and practicality aside, this new activation mode might offer a new opportunity to harness the

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synthetic applicability of amidyl radicals for building up molecular complexity. In this communication, we present evidences on (i) the formation of an anion-π complex between carbonate and an electron-poor N-aryloxyamide, (ii) the weakening of the N-O bond resulting from this interaction and (iii) the direct cleavage of this bond after single electron transfer (SET) induced by visible light, resulting in an amidyl radical that can be trapped in either intermolecular or intramolecular fashion by electron-rich aromatic substrates. As the first test of our hypothesis, we studied the behavior of the 2,4-dinitro substituted aryloxy amide 1a in the presence of K₂CO₃ in acetonitrile (ACN) solution. Interestingly, the UV-visible spectra showed the appearance of a dramatic enhancement in the absorption between 425 and 450 nm) (Figure 1, red trace). We next studied the light-promoted reaction (4.5 W blue LED, emission centered at 460 nm, see Supporting Information for further details) between 1a and N-methyl indole (2a) in the presence of K₂CO₃ as the sole additive (Table 1).



Figure 1. UV-visible absorption studies.

 Table 1. Screening and optimization of reaction conditions for the amidation of

 N-methylindole (2a) with 1a.



Entry	Variation from standard conditions ^[a]	Yield (%) ^[b]
1	None	75
2	Acetone instead of ACN	63
3	DMSO instead of ACN	68
4	1.5 equiv. of 2a	72
5	23 W CFL instead of blue LEDs	<5 ^[c]

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6	Green LEDs instead of blue LEDs	29 ^[d]
7	White LEDs instead of blue LEDs	37 ^[d]
8	No K ₂ CO ₃ , 48 h	18 ^[d]
9	No light	<5 ^[c]
10	NaH ₂ PO ₄ instead of K ₂ CO ₃	25 ^[d]
11	Na(PhO) ₂ PO ₂ instead of K ₂ CO ₃	31 ^[d]
12	(NEt ₄)HCO ₃ instead of K ₂ CO ₃	15
13	K ₂ HPO ₄ instead of K ₂ CO ₃	75
14	Na ₂ (PhO)PO ₃ instead of K ₂ CO ₃	75
15	K ₃ PO ₄ instead of K ₂ CO ₃	75
16	Et3N instead of K ₂ CO ₃	7
17	Cs ₂ CO ₃ in acetone instead of K ₂ CO ₃	50

[a] Standard conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), K_2CO_3 (0.4 mmol), ACN (2.0 mL) blue LEDs (4.5 W) r.t., overnight; [b] After flash column chromatography; [c] By ¹H NMR of the reaction crude. [d] Incomplete reaction (30% conversion).

We were pleased to observe that working under the standard conditions of Table 1 the reaction proceeded to completion overnight, affording the amidated indole **3a** in 75% yield (entry 1). The substitution of acetonitrile with other solvents such as acetone (entry 2) or DMSO (entry 3) lowered the yield (63 and 68%, respectively). Decreasing the ratio between **1a** and **2a** led to a slight erosion of the yield, as well (entry 4). The nature of the light source revealed to be determinant for the reaction outcome of the transformation. In fact, when either a compact fluorescence lamp (CFL), or green or white LEDs were employed, the reaction became much slower with consequent lower yields (entries 5, 6 and 7). Importantly, both the presence of carbonate and of a light source proved to be necessary for the success of the transformation. (entries 8 and 9, respectively).



Scheme 1. Intermolecular light-promoted amidaton

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The scope of this transformation was next investigated under the 1). optimal reaction conditions (Scheme Modifying the substituents of either the amide in 1 or of the N-substituted indole did not affect the reaction outcome. In fact, the corresponding amidated products **3a-3i** were isolated in good to high yields, and the same stands for **3j**, derived from *N*-phenylpyrrole. When switching to different aromatic carbocycles as partners, a decrease in yield was generally observed (3k-3n), with the notable exception of azulene, which afforded the amidated product 3o in high yield. Starting from 1,2-dimethyl indole and 1,2,3-trimethyl indole, the light-promoted amidation proceeds efficiently at C-3 (products **3p** and **3q**), leading in the second case to dearomatization. When 1,3,3-trimethyl-2-methyleneindoline (Fischer base) is used as radical acceptor, the amidation took place at the exo double bond, affording 3r in moderate yield and good diastereoselectivity. We next explored the possibility of an intramolecular version of the light-promoted amidation reaction, which would afford pharmaceutically valuable pyrroloindoline motifs **5** (Scheme 2).^[21] Inspired by a previous work by Wang and co-workers,[22] we synthesized compound 4, which was irradiated with blue LEDs in the sole presence of potassium carbonate (Scheme 2A). Although complete consumption of the starting material was observed, the desired compound 5a was not obtained. This experiment strongly suggests that the putative tertiary radical intermediate that could be originated by N-O cleavage from 4 is not able to reduce the starting material and, thus, the radical chain propagation step cannot take place. To circumvent this limitation, tert-butyl thiol and TEMPO were added to the reaction mixture as radical scavengers, affording the desired cyclized products **5b** and **5c** in 60% and 79% yield, respectively (Scheme 2B and 2C). Taking all these results into account, the tentative mechanistic proposal shown in Scheme 3 was formulated for an anion- π driven, light-induced amidation. Complex A, an anion-π complex generated by the interaction of the electron-poor aryloxyamide 1a with K2CO3, can be excited to A* by blue LED-light irradiation (Figure 1). This excited state can then undergo an intramolecular single electron transfer (SET) event, leading to the disassembly of the complex and generating the radical anion C, which readily fragments into the amidyl radical D and the phenolate E. The former can attack the *N*-methyl indole, affording radical F. This radical can contribute to the chain propagation^[23] by reducing **1a** (E_{red} = -0.26 V vs SCE) to the readily cleavable intermediate **C**^[18b] and giving rise to the carbocation species G, whose base-induced deprotonation leads to the amidated product 3a. Another intriguing possibility involves the reduction of radical B, which affords G from F regenerating the carbonate species.[24]



Scheme 2. Intramolecular light-promoted amidaton. Reaction conditions: blue LEDs (4.5 W), r.t., overnight. Yields measured after column chromatography. [a] The only isolated product was 1-Methylindole-3-carboxaldehyde (20% yield).

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Scheme 3. Proposed mechanism of the anion-π driven photo-amidation.

Although the anion- π interaction looks very relevant for the outcome of this transformation, an alternative mechanism could in principle be also operate in the observed transformation involving the homolytic cleavage of the N-O bond in 1a due to the absorption of light of the proper wavelength (see also the Supporting Information). The possible light-induced homolysis of 1a was tested (Scheme 4) by irradiating 1a in the standard conditions of this study (blue LED, 4.5 W) and in the presence of 1,4-cyclohexadiene (6). The formation of the homolysis products 7 and 8 under these conditions was observed by NMR, proving that also the homolytic cleavage could have some relevance in the reaction outcome. However, it is important to note that the possible contribution of this initiation mode appears to be rather unimportant, as shown by the results of the amidation reaction performed in the absence of base (Table 1, entry 8), where only a 18% yield of 3a is achieved after 48 h reaction.



Scheme 4. Study on the homolytical fragmentation of **1a**. Reaction conditions: **1a** (0.2 mmol), **6** (1.0 mmol), deuterated-acetonitrile (2.0 mL), blue LEDs (4.5 W), r.t. overnight. The conversion was measured by ¹H NMR.

At this point, it became important to assess the influence of the base used in the amidation reaction, for its fundamental role in the generation of the anion- π complex. From the observation of the results summarized in Table 1, entries 10-16, we can deduce that: i) the use of a neutral base, such as trimethylamine is deleterious for the transformation (entry 16), ii) the use of singly charged anions has a negative effect on the outcome of the reaction (entries 10-12), and iii) doubly or triply charged anions are those giving the best results (entries 13-15). Interestingly, these observations perfectly correlate with the expected strength of anion- π interactions.

In an attempt to perform photochemical studies on **A**, which would be facilitated by a high concentration of the complex, soluble tetrabutylammonium phosphate was used as the anionic component, since the use of caesium carbonate in acetone resulted deleterious (entry 17). However, when solutions of 1a and $(Bu_4N)_3PO_4^{[25]}$ in acetonitrile were mixed in an inert environment (glovebox), as well as in the dark, an immediate and complete decomposition of 1a took place, suggesting an extreme photochemical and thermal lability of A. To confirm these qualitative observations on the formation and lability of anion-π complex A, the ability of the different bases to form complexes with the substrate 1a was analysed by DFT calcu-lations at the B3LYP-D/6-311+G* level of theory. Firstly, the molecular electrostatic potential (MEP) was computed, plotted onto the Van der Waals surface in order to know which are the most electrophilic and nucleophilic parts of the substrate (Figure 2). The most negative region corresponds to the O atom of the carbonyl group (-30 kcal/mol, red colored). On the other hand, the electrostatic potential over the aromatic ring is positive (+23.8 kcal/mol, blue colored) due to the electron-withdrawing effect of both nitro groups. Therefore, the substrate is well suited to establish anion- π interactions. In addition, the H atom of the Nbonded methyl group that points to the aromatic surface also exhibits a large and positive MEP value (+30.7 kcal/mol, see Figure 1a). In summary, this MEP analysis anticipates that anionic bases will interact with the substrate by means of a combination of H-bonding and anion– π interactions.



Figure 2. Closed (a) and open (b) MEP surfaces of 1a.

Next, the EDA complexes of the 1a with monoanionic (hydrogencarbonate) and dianionic (carbonate) bases were computed both in the gas phase and taking into consideration solvent effects (using a polarized continuum model).[26] Key geometric features of the optimized geometries and interaction energies of the CT complexes are shown in Figure 3. As predicted by the MEP analysis, the complexes are stabilized by the concurrent formation of anion– π and H-bonding interactions in all cases (see Supporting Information). The corresponding equilibrium distances are shorter for the dianionic molecules because the electrostatic forces are stronger. Consequently, the interaction energies are significantly greater in absolute value for the dianionic bases. Thus, for all monoanionic complexes the interaction energies in acetonitrile range from -1.7 to -0.9kcal/mol (see also Supporting Information), while for the dianionic complexes the interaction energies are all very similar (around -5 kcal/mol). Interestingly, this correlates well with the ability of the different bases (Table 1) to promote the light-induced amidation and, in particular, with the observation that essentially the same yield (ca. 75%) is recorded for all the studied dianionic bases. From the geometrical point of view, it is important to remark that the N–O distance increases upon formation of the EDA complex. The N–O distance in 1a is 1.42 Å, which goes up to 1.43 Å in all EDA complexes, thus revealing a weakening of the N-O bond upon complexation.

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Figure 3. B3LYP-D/6-311+G* optimized geometries and energies of the bicarbonate (a) and carbonate (b) complexes of 1a. Distances in Å.

A key point in our mechanistic hypothesis is the absorption of one photon by complex **A** leading to the generation of the excited state A^* , where an internal SET can take place. When the frontier orbitals of complex **A** are analyzed, it can be observed (Figure 4) that the HOMO is located in the anion region (a), while the LUMO is concentrated in the nitro groups and one carbon atom of the aromatic group. The very small computed HOMO-LUMO difference (1.83 eV) anticipates that low-lying excited states are available for this structure, and that internal single electron transfer should be quite feasible.



Figure 4. Plots of the HOMO (a) and LUMO (b) of complex A. (c) Spin density plot of the biradical open singlet configuration of A.

Moreover, since small HOMO-LUMO gaps are indicative of biradical or biradicaloid character, we examined the presence of this character in A. To do so, the electronic structure of the complex was re-calculated using an open-shell singlet configuration, this leading to an energy drop of 1.4 kcal/mol (i.e.; the biradical is predicted to be more stable than the closed-shell system). The spin density plot of this configuration is depicted in Figure 4c and it clearly shows that the alpha electron (blue) is located basically in the aromatic ring and nitro groups, whereas the beta electron is located in the carbonate. It thus corresponds to a situation where an internal SET has taken place from the putative complex A*. It is worth to comment that the attempted geometrical optimization of this configuration leads to the dissociation of the complex because of the mutual electrostatic repulsion of two negative charges [CO3⁻⁻ ----1a⁻⁻]. Interestingly, the optimized structure of C (1a⁻⁻) exhibits an elongation of the N-O bond with respect to 1a (Figure 5).

Additional data from two different origins further confirm the relevance of the anion- π complex in the light-mediated cleavage of **1a**. First, the results of time-dependent DFT calculations show that the presence in **A** of the anion interacting with the π -system

of **1a** increases the probability of excitation and decreases the absorption energy (see Supporting Information).



Figure 5. Optimized structure of C (distance in Å).

Second, when the homolysis of the N–O bond required for the generation of the amidyl radical **D** is considered, it is found that the direct homolysis of **A** yielding carbonate dianion and radicals **H** and **D** is not energetically favorable (52.2 kcal/mol), being almost identical to the calculated for **1a** (54.7 kcal/mol, Supporting Information). In contrast, the transformation of **A** to **C** with the concomitant formation of $[CO_3^-]$ is more achievable $[\Delta G_r(\mathbf{A} \rightarrow \mathbf{C}) = 6.1 \text{ kcal/mol}]$ and, remarkably, the subsequent homolysis of the transient intermediate **C**, yielding **D** and **E** is predicted to be exergonic $[\Delta G_r(\mathbf{C} \rightarrow \mathbf{D} + \mathbf{E}) = -10.6 \text{ kcal/mol}]$. The calculated activation energy for this homolysis step is very low, i.e. $\Delta G_{act} = 3.2 \text{ kcal/mol}$, thus confirming the feasibility of this mechanistic route (see Supporting Information for further details).



Scheme 5. Energetics of the calculated generation of amidyl radical D from anion– π complex A.

In conclusion, anion- π interactions have been identified for the first as an enabling phenomenon in light-mediated processes. Anion- π interactions involving carbonate anion have been described by spectroscopic and theoretical methods as the enabling step in the light-promoted amidation of arenes with activated aryloxyamides. The available evidence supports the hypothesis that π -interactions between carbonate and the electron-poor aryloxyamide facilitate the absorption of visible light (blue LED) promoting the generation of a low-lying excited state that spontaneously experiences internal SET and disintegration of the complex, providing a low-energy pathway for the generation of highly reactive amidyl radical. Our results suggest that other

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poorly understood light-promoted processes involving the use of inorganic bases can also result from overlooked anion- $\!\pi\!$ interactions.

Experimental Section

The corresponding aryloxyamide **1** (0.2 mmol) was mixed in a 10 mL vial with K_2CO_3 (0.4 mmol, 55 mg) and an aromatic compound **2** (if solid) (0.4 mmol). Then the vial was sealed and three cycles of vacuum-refill with Ar were performed. After adding ACN (2.0 mL) and degassing with a flow of argon during 10 minutes, the aromatic compound **2** (0.4 mmol) was added with a syringe (when liquid) and the mixture was stirred under blue LEDs (4.5 W) irradiation overnight. Afterward, it was washed with water (5.0 mL), extracted with EtOAc (3x4.0 mL) and dried over MgSO₄. The reaction mixture was then filtered and concentrated under vacuum. The desired

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Entry for the Table of Contents (Please choose one layout)

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Largelyoverlooked,theformationofanion-πcomplexestriggerslight-mediatedprocessesbyfacilitatingphotonabsorptionandintramolecularsingleelectrontransfer



Anion- π complexes: Hidden landmarks on the way to photogenerated amidyl-radicals

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