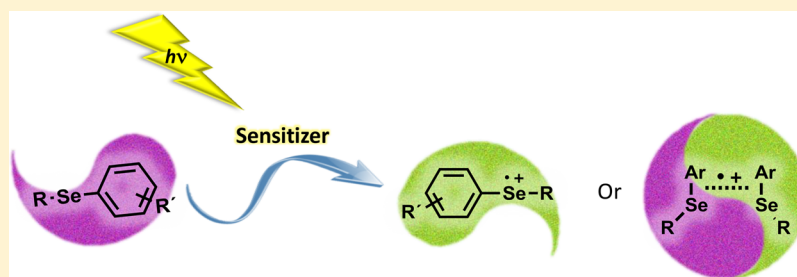# Photoinduced One-Electron Oxidation of Aromatic Selenides: Effect of the Structure on the Reversible Dimerization Reaction

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**S** *Supporting Information*

**ABSTRACT:** The photochemical one-electron oxidation of alkyl aryl selenides was studied by means of laser flash photolysis (355 nm). Quenching of the sensitizers in their excited state leads to selenide radical cation in the presence of selenium derivatives. The $\pi$-type dimer of methyl phenyl selenide radical cation was detected at 630 nm at expenses of the monomeric radical cation (530 nm). The effect of modification of the aryl and alkyl substituents was also studied, resulting that the formation of dimers depends on both, the electronic properties and steric hindrance of the substituents. Both effects, an increase in steric hindrance in the alkyl moiety or the presence of strongly electron donor groups in the aromatic substituent that stabilizes the radical cation, prevent the dimer formation.

## INTRODUCTION

Over the last years, selenium compounds have become very attractive in many fields such as medicine, biology, and material science.[1] Selenium is an essential element for animals and humans as micronutrient, as well as playing a central role in the active site of enzymes; an example of this is selenocysteine, which is an essential part of the redox enzyme glutathione peroxidase (GPx), a very well-known radical oxygen species (ROS) scavenger in the antioxidant defense mechanism.[2] Moreover, until now 25 selenoproteins have been identified in humans,[3] together with a large number of organoselenium compounds that have also been demonstrated to mimic the GPx like activity, catalyzing the reduction of hydrogen peroxide, a molecular oxidant and ROS.[4] In general, antioxidants act by arresting the deleterious effect of free radicals and molecular oxidants, which are important intermediates in oxidative stress. In turn, selenium compounds exhibit antioxidant and anti-inflammatory activity and are able to trap free radicals.[5] In consequence, the redox properties as well as the nature of the oxidized species of selenium compounds are in continuous study, and understanding such processes is necessary to exploit future applications of selenium compounds.

Since selenium and sulfur belong to the same family, i.e., group 16 of the periodic table, selenium compounds are expected to participate in chemical reactions in a manner similar to that of sulfur compounds. In this matter, formation and dynamics of sulfide radical cations are extensively explored by means of pulse radiolysis and laser flash photolysis techniques.[6] To a lesser extent, a number of water-soluble aliphatic selenide compounds were also studied by radiolytic methods.[7] A comprehensive comparison between parent alkyl sulfide and selenide radical cations have been reported by Asmus et al.,[8] together with selenomethionine in comparison with methionine.[9] However, to the best of our knowledge only two reports on diarylselenides and aryl methyl selenides radical cations have been described by pulse radiolysis, which is an excellent technique to induced short-lived free radical species formation, although limited to relatively small, water-soluble selenides.[6c,10]

Settled in our experience on the selenide radical chemistry[11] and sulfide radical cation chemistry,[12] we determined the effect of the aryl and alkyl substituents on the formation and reactivity of selenide radical cations. Moreover, spectroscopic, kinetic, and thermodynamic properties of these radical cations were studied by means of laser flash photolysis (LFP) which is a powerful technique to follow one-electron induced redox processes in real time. For this, alkyl aryl selenides (Chart 1) having different substituents on the aromatic ring (**1−5**) as well as different alkyl substituents (**1, 6−7**) are studied in the present report.
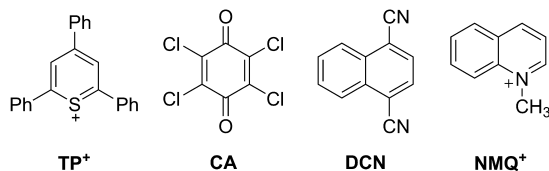
**Chart 1. Alkyl Aryl Selenides Studied, Sensitizers and Co-Sensitizer Used**

**Alkyl Aryl Selenides**

**Sensitizers**

**TP+**   **CA**   **DCN**   **NMQ+**

**Co-Sensitizer**

**BP**
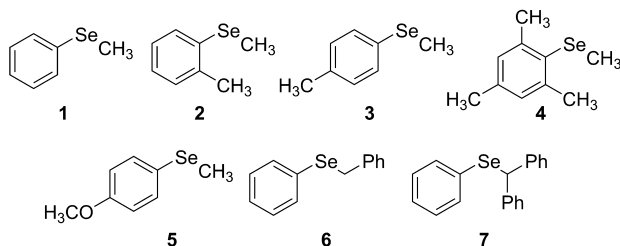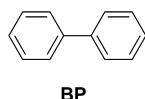
## ■ RESULTS AND DISCUSSION

The photoinduced electron transfer reaction is an accurate strategy to form selenide radical cations, well-established by Pandey et al.[13] Therefore, we have investigated, through the LFP technique, the formation of radical cations of aromatic selenides using different sensitizers. Also, we evaluated the effect of the concentration of selenium derivatives on the properties of these radical cations, thus determining if dimer formation occurs.

**Photosensitized One-Electron Oxidation of Methyl Phenyl Selenide (1).** The laser flash photolysis excitation ($\lambda_{exc}$ = 355 nm) of 0.06 mM 2,4,6-triphenyl thiapyrylium perchlorate dye (**TP+**) in argon-saturated acetonitrile solution in the presence of 1 mM methyl phenyl selenide (**1**) resulted in the quenching of the **TP+** triplet. The quenching constant was determined using the Stern−Volmer equation[14] and was found to be $1.09 \times 10^{10}$ M$^{-1}$ s$^{-1}$, which indicates that selenide **1** deactivates **TP+** triplet at a diffusion-controlled rate which is in agreement with the highly exergonic photoinduced electron transfer free energy changes estimated by the Weller equation[14] (Figure S1 and Table S1). Moreover, this process was followed by the appearance of a new broad transient band with maximum absorption at 630 nm (Figure 1, blue ▲), which would be assigned to semioxidized methyl phenyl selenide (**1•+**) generated by electron-transfer from the ground state of **1** to excited **TP+**. The formation of **1•+** was previously reported by means of pulse radiolysis.[6a] This radical cation showed a maximum at 560 nm. The typical absorption of **1•+** could not be observed under our experimental conditions. However, to evaluate the radical cation nature of the observed transient, other one-electron photosensitizers, chloranil (**CA**), 1,4-dicyanonaphthalene (**DCN**), and *N*-methylquinolinium tetrafluoborate (**NMQ+**), were evaluated in the presence of **1** under laser excitation (Figure 1). In all cases, the transient with a maximum at 630 nm was always observed. The fluorescence of **DCN** and **NMQ+** is efficiently quenched by **1** via diffusion-controlled processes for both sensitizers (see Figures S2 and
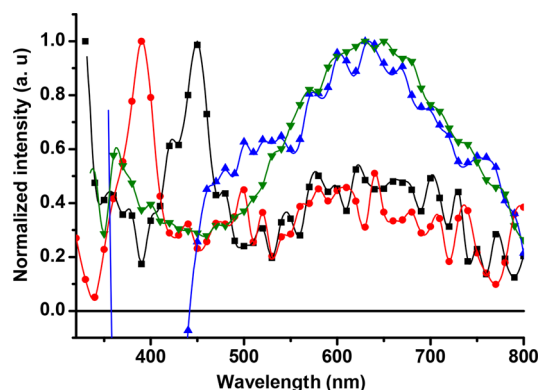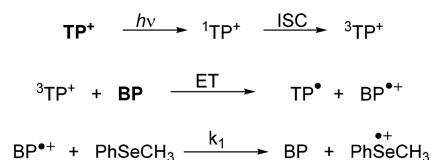


**Figure 1.** Transient absorption spectra under argon observed at 1 μs after the laser excitation (355 nm) of argon-saturated acetonitrile solutions of 0.06 mM **TP+** (blue ▲), 1 mM **CA** (black ■), 0.25 mM **DCN** (red ●), 3.4 mM **NMQ+** (green ▼) in the presence of 1 mM of methyl phenyl selenide (**1**).

S3). Moreover, triplet quenching of **CA** resulted in a second band with a maximum at 450 nm which is assigned to chloranil radical anion (**CA•−**) form (Figure 1, black ■).[15] The quenching of the fluorescence of **DCN** and **NMQ+**, with the addition of **1**, led to the formation of new bands at 390 and 550 nm, respectively, which correspond to the reduced form of the sensitizers (Figure 1, red ● and green ▼ for **DCN•−** and **NMQ•**, respectively). Under oxygen atmosphere, the absorption of **NMQ•** rapidly decayed by secondary electron transfer toward oxygen to form O$_2$•−,[16] while the species with $\lambda_{max}$ = 630 nm remains practically unaffected by the presence of molecular oxygen. The presence of the reduced form of the sensitizers after laser excitation together with the lack of reactivity toward molecular oxygen are consistent with an electron transfer process, where the radical cation species are formed by one-electron oxidation of **1**. However, we believe that the transient observed does not correspond to the monomer radical cation **1•+** but rather to its dimer form.

Considering that selenide-centered radical cations are able to form dimers in the presence of a neutral selenide molecule, the dependence on concentration (from 0.1 to 10 mM) of **1** was examined during its photooxidation in the presence of 0.06 mM **TP+** and 100 mM biphenyl as co-sensitizer (**BP**), in argon-saturated solution of acetonitrile at 20 °C. **BP** was added as a hole mediator which not only quenches $^3$**TP+** efficiently but also improves charge separation. Moreover, diffusion-controlled hole transfer from **BP•+** to **1** is then possible and offers the possibility to evaluate the selenide radical cation concentration up on laser excitation (Scheme 1). At lower concentrations of **1** (0.25 mM, Figure 2a, black ■) a new transient band centered at 530 nm was observed. When the concentration of **1** was increased to 0.5 mM, the intensity of the band at 530 nm slightly decreases, and the transient at 630 nm begins to be observed (Figure 2a, red ●). At higher concentrations (5 mM,

**Scheme 1. Formation of 1•+ by Photoinduced ET Process Using TP+ and BP**

$$\text{TP}^+ \xrightarrow{h\nu} \, ^1\text{TP}^+ \xrightarrow{\text{ISC}} \, ^3\text{TP}^+$$

$$^3\text{TP}^+ + \text{BP} \xrightarrow{\text{ET}} \text{TP}^\bullet + \text{BP}^{\bullet+}$$

$$\text{BP}^{\bullet+} + \text{PhSeCH}_3 \xrightarrow{k_1} \text{BP} + \overset{\bullet+}{\text{PhSeCH}_3}$$
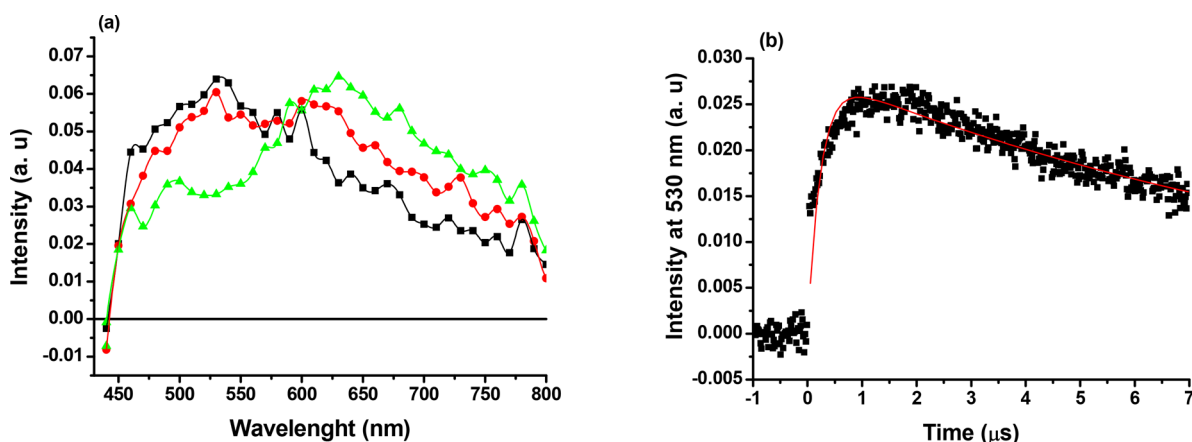
**Figure 2.** Transient absorption spectra after the laser excitation (355 nm) on argon-saturated acetonitrile solution. (a) Effect of concentrations of **1** on the transient absorption spectra observed at 0.3 $\mu$s after the laser excitation of 0.06 mM **TP$^+$**, 100 mM **BP**, and 0.25 (black ■), 0.5 (red ●), and 5 (green ▲) mM of selenide **1**. (b) Decay kinetic trace monitored at 530 nm after laser excitation of **1** (0.1 mM) in the presence of 0.06 mM **TP$^+$** and 100 mM **BP**.

Figure 2a, green ▲), the band at 530 nm completely disappears, and the only species that remains is the one at 630 nm, as in the case 1 mM of **1** (Figure 1, blue ▲). Even dicationic dimer coming from the recombination of two radical cations has been observed by positive ion mode ESI mass spectrometry[17] and electron paramagnetic resonance in solid state;[18] under our experimental conditions, where the dimer radical cation is stabilized by polar acetonitrile in solution, this process is unlikely.

An isosbestic point can be observed at 580 nm, which indicates that the band at 530 nm is the immediate precursor of the species that appears at 630 nm. Therefore, the experiments indicate that the band at 530 nm corresponds to monomeric **1$^{•+}$**, in agreement with pulse radiolysis results,[6a] while the band centered at 630 nm is assigned to the dimer (**D$^{•+}$**), formed between the radical cation and a neutral molecule **1** (Scheme 2). The absence of dimers in the pulse radiolysis studies could

**Scheme 2. Dimer Formation of 1$^{•+}$**
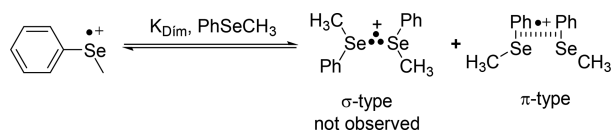


be attributed to the low concentration of methyl phenyl selenide limited by the low solubility of aryl selenides in aqueous media.

Decay kinetic trace monitored at 530 nm showed that the formation of **1$^{•+}$** in the presence of biphenyl and **TP$^+$** is not instantaneous at low concentrations of **1** (0.1−0.25 mM, Figure 2b). Also, two distinctive regions can be observed in Figure 2b: At the first stage, formation of **1$^{•+}$** takes place in the first microsecond after the laser pulse; kinetic information can be extracted by fitting the trace to an apparent rate constant ($k_1 \times$ [**1**]) from the grow of the signal, followed by the decay of **1$^{•+}$** with a constant $k_2$. This latter kinetic rate constant accounts for all the decay processes of the radical cation, namely, $\alpha$-deprotonation, C−Se bond fragmentation, or return electron transfer to the thiapyranyl radical. The plot of the apparent rate constant against selenide concentration gives $k_1$ (Figure S4) where a linear behavior is observed with a slope value of 5 × $10^{10}$ M$^{-1}$ s$^{-1}$. This value corresponds to the formation constant

of **1$^{•+}$** which is in good agreement with the deactivation constant of **BP$^{•+}$** (2.25 × $10^{10}$ M$^{-1}$ s$^{-1}$) previously measured and unambiguously confirms the formation of **1$^{•+}$** by an ET process (Scheme 1).

One of the frequent reactions of radical cations is the formation of dimers, which involves association of a radical cation with a neutral parent molecule. Such dimers can be divided into two types, $\sigma$ or $\pi$. For the former, the nature of interaction results in the formation of a new $\sigma$ bond of three electrons and two centers, containing two bonding $\sigma$ electrons and one antibonding $\sigma^*$ electron.[19] For organoselenide compounds, since the electron density is mostly located in the selenium atom and it has a low ionization potential, the radical cations are expected to be selenium centered. This species, like their sulfur analogs, is generally unstable, so it tends to stabilize through the coordination of the unpaired electron from the radical cation with a pair of electrons from a second selenium atom or another heteroatom in the molecule.[7b] Examples of $\sigma$-type dimers are aliphatic selenide radical cations which are stabilized by forming Se−Se two-centered three-electron bonded dimer radical cations that absorb in the region below 500 nm due to the $\sigma−\sigma^*$ transition.[7a,d,f,9b,20] In contrast, $\pi$-type interaction results from the stabilization of the radical cation by charge resonance $\pi$ interaction with a neutral molecule ($\pi$-stacking interactions). For the best of our knowledge, this type of interactions has never been reported yet in selenide radical cations.

For aliphatic selenides, only $\sigma$ dimer radical cations have been reported, where its $\sigma−\sigma^*$ transition lies in the visible region as a broad absorption band centered at wavelengths around 500 nm,[7a,d,9b,20c] while for the sulfur analogue, thioanisole radical cation, the typical absorption band for the monomer is observed at 520 nm. At higher concentrations (over 10 mM), two new bands at 470 and 800 nm appeared, assigned as $\sigma$ and $\pi$ dimers, respectively.[21] Since the transient absorption spectrum of thioanisole and methyl phenyl selenide radical cations resemble each other, we assigned the absorption bands at 530 and 630 nm as the monomer and $\pi$-type dimer of **1$^{•+}$**, respectively. Moreover, the concentration experiment indicated in Figure 2a is in good agreement with the equilibrium reaction indicated in Scheme 2 where $\sigma$ dimer has not been observed even at high concentrations of **1**.
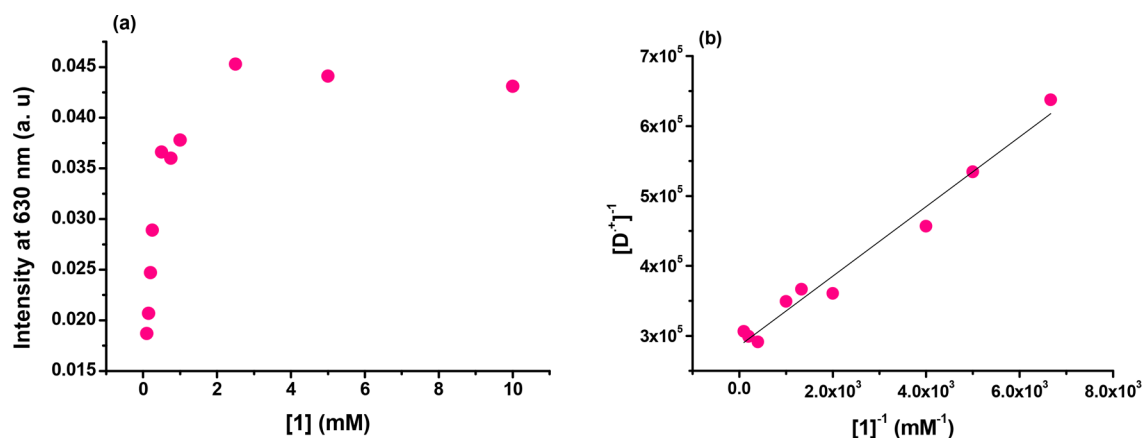
**(a)**



**(b)**

**Figure 3.** (a) Plot of the absorbance of $D^{\bullet+}$ at 630 nm against the concentration of **1**; (b) double reciprocal plot of the concentration of $D^{\bullet+}$ as a function of **1** according to eq 2, at 20 °C. Slope obtained after linear fit of experimental data, $R^2 = 0.973$.

**Table 1. Spectroscopic Characterization of Alkyl Aryl Selenide Radical Cations**[a]

| entry | alkyl aryl selenide | $\lambda_{maxArSeR\bullet+}$ (nm) | $\lambda_{maxD\bullet+}$ (nm) | $K_{D\bullet+}$ (M$^{-1}$)[b] | $\varepsilon_{D\bullet+}$ (M$^{-1}$ cm$^{-1}$)[c] |
|---|---|---|---|---|---|
| 1 | **1** | 530 | 630 | $(6 \pm 1) \times 10^3$ | $1.3 \times 10^4$ |
| 2 | **2** | 530 | 710 | $(4.1 \pm 0.2) \times 10^3$ | $8.3 \times 10^3$ |
| 3 | **3** | 530 | 720 | $(3.2 \pm 0.5) \times 10^3$ | $6.1 \times 10^3$ |
| 4 | **4** | 600 | d | | |
| 5 | **5** | 640 | d | | |
| 6 | **6** | 520 | 630 | $(6 \pm 2) \times 10^3$ | $1.0 \times 10^4$ |
| 7 | **7** | 600 | d | | |

[a]After laser excitation of 0.06 mM **TP**$^+$, 100 mM **BP** in argon-saturated acetonitrile at 20 °C. [b]Determined according eq 2. [c]Determined by Farid's hole-transfer method. [d]Dimer was not observed.

**Estimation of the Binding Constant.** The equilibrium constant ($K_{D\bullet+}$) for the dimer formation was determined by eq 2, the double reciprocal of eq 1, where $[D^{\bullet+}]$ and $[D^{\bullet+}]_\infty$ are the concentration of the dimer at any given concentration of **1** and the saturating concentration of the dimer, respectively.

$$[D^{\bullet+}] = \frac{K_D[D^{\bullet+}]_\infty[1]}{1 + K_D[1]} \quad (1)$$

$$\frac{1}{[D^{\bullet+}]} = \frac{1}{K_D[D^{\bullet+}]_\infty[1]} + \frac{1}{[D^{\bullet+}]_\infty} \quad (2)$$

To obtain $K_{D\bullet+}$, the extinction coefficient of the dimer ($\varepsilon_{D\bullet+}$) was first estimated by Farid's hole transfer method.[22] Since absorbances are proportional to their concentrations, the dimer absorption was measured from the top OD monitored at 630 nm and plotted against concentration of **1** (Figure 3a) where a saturation behavior was determined (0.046). Taking this value together with the concentration of **BP**$^{\bullet+}$, an $\varepsilon_{D\bullet+}$ value equal to 1.32 × 10$^4$ M$^{-1}$ cm$^{-1}$ was obtained for the dimer. This value is slightly higher than that reported for thioanisole $\pi$ dimer radical cation ($\varepsilon = 1 \times 10^4$ M$^{-1}$cm$^{-1}$),[21] which is in agreement with the fact that selenides have higher absorbances than their sulfur analogues.[7b]

The plot of $1/[D^{\bullet+}]$ versus $1/[1]$ gave a straight line (Figure 3b) with a slope equal to $1/K_D[D^{\bullet+}]_\infty$, according to eq 2. The resulting equilibrium constant was $(6 \pm 1) \times 10^3$ M$^{-1}$. This value is significantly higher than the reported value of $(1.0 \pm 0.3) \times 10^2$ M$^{-1}$ for its sulfur analogue, thioanisole, in acetonitrile.[21] This difference could be attributed to the fact that radical cation **1** has higher electron density localized in the selenium atom and lower ionization potential than its sulfur

analogue.[6a] This results in **1**$^{\bullet+}$ having a lower stability than its sulfur analogue and a greater tendency to form dimers. Accordingly, for compound **1** the band corresponding to the dimer was observed at concentrations greater than 0.5 mM, while in the case of the sulfur compound, the dimer was observed at concentrations higher than 10 mM. For this reason, an acceptable $\varepsilon$ value for the monomer **1**$^{\bullet+}$ could not be obtained.

**Photosensitized One-Electron Oxidation of Aromatic Selenides.** The photooxidation of compounds **2**–**7** was likewise investigated in the presence of 0.06 mM **TP**$^+$ as photosensitizer and 100 mM **BP** as co-sensitizer in an argon–saturated acetonitrile solution at 20 °C. Compounds **2**–**5** are derivatives of **1** that have different substituents on the aromatic ring, while **6** and **7** have different aliphatic substituents. In all cases, the deactivation constant of triplet **TP**$^+$ was determined using the Stern–Volmer equation (see Table S1) where a diffusion-controlled rate quenching process was observed.

For the o-methylphenyl methyl selenide and p-methylphenyl methyl selenide (**2** and **3**, respectively) the LFP excitation measured at concentrations lower than 0.5 mM led to the production of a transient absorption intermediate with a maximum at 530 nm after the laser excitation (entry 2 and 3, Table 1 and Figure S5). These results are in agreement with the value reported for the monomeric form of **2**$^{\bullet+}$, obtained by pulse radiolysis.[10] When the irradiation was performed at higher concentrations of **2** and **3**, a drastic decrease in the absorbance of the band at 530 nm was observed, with the concomitant formation of a new band centered at 710 and 720 nm, respectively. An isosbestic point is observed at 600 nm for **2** and at 610 nm for **3**. Since the absorption at 530 nm decreased with the increasing concentration of selenides, it is

D

reasonable to suppose that this band correspond to **2** and **3** radical cations. However, those appearing at higher wavelengths and concentrations of selenides correspond to the dimer radical cations. For both compounds, the equilibrium constant for dimer formation was determined, with values of $(4.1 \pm 0.2) \times 10^3$ M$^{-1}$ for **2** and $(3.2 \pm 0.5) \times 10^3$ M$^{-1}$ for **3** (entries 2 and 3, Table 1). Therefore, the presence of a weak electron donor group in the aromatic ring as a methyl group that stabilizes the radical cation, produces only a small decrease in the equilibrium constant for the dimer formation. We assume that these dimers are of $\pi$-type nature based on the region where the maximum absorption of both transients was observed, similar to **1**, and no evidence of the $\sigma$-type was observed on the concentration range studied. Also, it was found that the position of the substituent, *ortho-* or *para-*, does not influence significantly the value of the equilibrium constant. Thus, the decrease of $K_{D\bullet+}$ compared to that of **1** was attributed to the modification of electronic properties produced by the substitution of the aromatic ring and not to steric hindrance produced by the small methyl group. The addition of a weak donor group in the aromatic ring stabilizes only by inductive effect the $\pi$-system delocalized positive charge; however, this effect is not enough to avoid the dimer formation. In addition, since a small difference, within the experimental error, in the $K_{D\bullet+}$ values by *ortho-* or *para-* substitution was observed, we assume that there is not significant steric hindrance effect between methyl groups of the aromatic rings in the $\pi$-type dimer radical cation.

For mesityl methyl selenide (**4**) and *p*-methoxyphenyl methyl selenide (**5**), the transient absorption was observed at 600 and 640 nm, respectively; both spectra remained unaffected even at selenide concentrations over 10 mM (entries 4 and 5, Table 1, Figure S6). These bands were assigned to corresponding monomeric radical cation species **4$^{\bullet+}$** and **5$^{\bullet+}$**, and no dimer radical cation was evidenced for selenides **4** and **5** on the concentration range been used. This could be attributed to the increase of the radical cation stability due to the presence of strong electron-donating groups, such as one $-OCH_3$ or three $-CH_3$, in the aromatic ring. The presence of these groups result in a greater delocalization of the positive charge over the aromatic ring in a more effective way compared to that in selenides **1−3**. This behavior was also observed for the sulfur analogue of **5**, *p*-methoxythioanisole, under photoinduced electron transfer conditions[21] and for the *o*-$CH_2N(CH_3)_2C_6H_4$ methyl selenide in pulse radiolysis experiments. For the latter, the great stability of the radical cation and the absence of the dimer were attributed to the strong Se$\cdots$N nonbonding intramolecular interaction.[10]

Modification in the alkyl moiety of the selenide keeping phenyl as aryl substituent was also evaluated. In the case of benzyl phenyl selenide (**6**), the resulting spectra showed an absorption maximum centered at 520 nm at low selenide concentration, while above 0.5 mM of **6**, the OD at 520 nm decreased and a new band at 630 nm was formed (entry 6, Table 1, Figure S7 a). The former transient band was assigned to **6$^{\bullet+}$** while the latter corresponds to the dimer formed with an equilibrium constant estimated on $(6 \pm 2) \times 10^3$ M$^{-1}$. Finally, for diphenylmethyl phenyl selenide (**7**), with a diphenyl-methane moiety instead of a methyl group as aliphatic substituent, a single band with a maximum at 600 nm was observed over the entire range of concentrations measured, such band was assigned to the monomeric radical cation (entry 7, Table 1, Figure S7 b). From alkyl change modification study, it was found that transient absorption spectra taken by means

of LFP and $K_{D\bullet+}$ were practically the same for selenides **1** and **6**. Whiting the experimental error, we have found that a $CH_3$ by a $PhCH_2$ modification in the alkyl side of the molecule produced no change in either the stability or in the electronic environment and did not generate enough steric hindrance to prevent the dimer formation of the selenide radical cation. In contrast, when the methyl group was replaced by a diphenylmethyl group, the dimer formation was not observed at all due to a greater steric hindrance introduced by the second aromatic ring in the aliphatic substituent that avoids the dimer formation.

## CONCLUSION

The alkyl aryl selenides studied quench **CA** and **TP$^+$** triplet state as well as **NMQ$^+$** and **DCN** singlet state with quenching rate constants close to the diffusion-controlled limit. The agreement between the kinetics together with the observation of **CA$^{\bullet-}$**, **DCN$^{\bullet-}$**, and **NMQ$^{\bullet}$** by LFP experiments confirm the electron transfer nature of the quenching process. Also, it was possible to detect, in real time, the presence of aromatic selenium-centered radical cations together with its $\pi$-type dimer, and its corresponding dimerization constants were measured for the first time. It was also found that dimer formation for compounds **1−7** depends on both the electronic properties and steric hindrance of the substituents. A clearly steric effect was triggered by the change in the alkyl substituent by bulky phenyl groups, whereas the electronic properties of the system can be modified by the inclusion of mesomeric ($-OCH_3$) or three inductive ($-CH_3$) electron donors groups on the aromatic ring. Therefore, an increase in steric hindrance in the alkyl substituent prevents the formation of the dimer, whereas the presence of strong electron donor groups in the aromatic substituent stabilizes the radical cation inhibiting dimer formation.

## EXPERIMENTAL SECTION

**General Methods.** $^1H$, $^{13}C$, and $^{77}Se$ NMR spectra were registered on a 400 MHz spectrometer (Bruker FT-400), and all spectra were reported in $\delta$ (ppm) relative to Me$_4$Si, with CDCl$_3$ as solvent. Measurements were carried out using the standard pulse sequences. GC-MS analyses were performed on a Shimadzu CG-EM QP 5050$^a$ spectrometer employing a 30 m $\times$ 0.25 mm $\times$ 0.25 $\mu$m with a 5% phenylpolysiloxane phase column. Ionization was achieved by electronic impact (70 eV) and detection setup on positive mode.

**Chemicals.** Chloranil, 1,4-dicyanonaphthalene and biphenyl were commercially available. Acetonitrile, acetone, ethyl ether and dichloro-methane were used as purchased without any further purification and stored over molecular sieves (4 Å). Ultrapure water from a Milli-Q station was used. Thiapyrylium perchlorate salt,[23] N-methylquinoli-nium tetrafluoborate,[24] and selenides $(1−7)$[25] were synthesized and purified according to the previously reported procedures.

**Spectroscopic Measurements by Laser Flash Photolysis (LFP).** All measurements were carried out under inert atmosphere, in quartz cell, and 20 °C. Transient absorption spectra, quenching rate and dimerization constants were determined using a Nd:YAG laser (Surelite I-10 of Continuum) generating 355 nm laser pulse (ca. 10 ns pulse duration) as excitation source. The spectrometer was a commercial setup.

## ASSOCIATED CONTENT

**Ⓢ Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b00684.

Fluorescence quenching of **DCN** and **NMQ$^+$** by **1**; transient spectra obtained upon LFP of **2-7**; quenching of **TP$^+$** triplet by **1**; rate constant for triplet quenching of **TP$^+$** ($k_q$) and estimated $\Delta G°_{ET}$ (PDF)

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**Notes**
The authors declare no competing financial interest.

## ■ DEDICATION

This paper is dedicated to the memory of Adriana Beatriz Pierini 1953−2016.

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