# Charge–transfer excitation of electron donor–acceptor complexes of arylcyclopropanes

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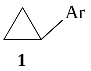
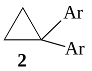
**Electron-transfer (ET) reactions of mono- and di-arylcyclopropanes 1 and 2 have been investigated by employing charge-transfer (CT) excitation of their electron donor–acceptor (EDA) complexes with tetracyanoethylene (TCNE) or *p*-chloranil (CA). For the TCNE complexes, no reaction is observed following photoexcitation within their CT bands. Picosecond absorption spectroscopic experiments with phenylcyclopropane 1a and 1,1-diphenylcyclopropane 2a reveal that the photogenerated ion radical pairs [1a$^{\bullet+}$, TCNE$^{\bullet-}$] and [2a$^{\bullet+}$, TCNE$^{\bullet-}$] are too short-lived to undergo chemical reaction. For the CA complexes, net chemical change is observed in the CT excitation of the 2a–CA complex though the efficiency is very low. The other arylcyclopropane–CA complexes are found to be unreactive. Factors concerned with the reactivity of 1 and 2 upon their CT-excitation are discussed.**

Electron-transfer (ET) reactions of organic strained-ring compounds have received considerable attention for more than 10 years.[1] Cyclopropane and its derivatives are among the most noteworthy compounds. Indeed, there have been numerous theoretical[2] and experimental[3–15] studies on the structures and reactivities of cyclopropane cation radicals. Photoinduced ET[16] has often been utilized to generate cation radicals of cyclopropane derivatives and they are found to undergo a variety of reactions such as isomerization,[7e,8–12] cycloaddition,[13] oxygenation[11,14] and nucleophile-assisted ring cleavage.[7d,13d,e,15]

Earlier investigations revealed that some cyclopropane derivatives undergo thermal [2σ + 2π] cycloadditions with electron-deficient alkenes.[17–19] For example, 1,1-diphenylcyclopropane thermally reacts with tetracyanoethylene (TCNE) to give 3,3-diphenylcyclopentane-1,1,2,2-tetracarbonitrile and its acyclic isomer.[18a] Since it is well known that TCNE forms weak electron donor–acceptor (EDA) complexes with arene donors, charge-transfer (CT) interactions might play an important role in these reactions. It is conceivable that the transition state has ion–radical pair character because of strong CT interaction between the cyclopropane donor and TCNE developed along the reaction coordinate. However, little is known about the role of the cyclopropane EDA complex.



**1**



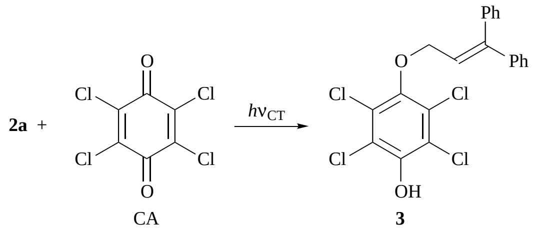
**2**

**a** Ar = phenyl
**b** Ar = 4-methylphenyl
**c** Ar = 4-methoxyphenyl
**d** Ar = 1-naphthyl
**e** Ar = 2-naphthyl

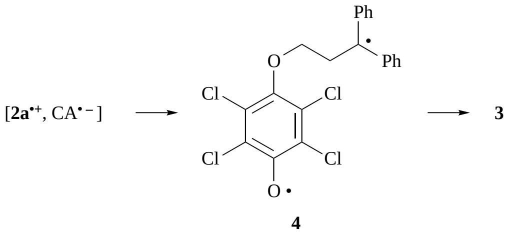
**a** Ar = phenyl
**b** Ar = 4-methoxyphenyl

Optical excitation (CT excitation) of weak EDA complexes derived from electron donors (D) and acceptors (A) results in ET from D to A to generate ion radical pairs [D$^{\bullet+}$, A$^{\bullet-}$] directly.[20,21] We undertook an exploratory study on the ET reactions of arylcyclopropanes **1** and diarylcyclopropanes **2** by CT excitation of their EDA complexes with TCNE and *p*-chloranil (CA). Such a study should provide insight into the nature of the ion radical pairs and also give an approach to understanding the reactivity of arylcyclopropane cation radicals.

$$\mathrm{D + A} \rightleftharpoons [\mathrm{D, A}] \underset{k_{\mathrm{bet}}}{\overset{h\nu_{\mathrm{CT}}}{\rightleftharpoons}} [\mathrm{D}^{\bullet+}, \mathrm{A}^{\bullet-}] \qquad (1)$$



(2)



(3)

## Results

### Formation of the EDA complexes of arylcyclopropanes 1 and 2

Arylcyclopropanes **1** and **2** are good electron donors and form EDA complexes with TCNE. When colourless solutions of TCNE in methylene chloride were mixed with **1** and **2**, orange to purple colourations were observed. The colour changes are due to the appearance of the CT absorption bands of the resulting EDA complexes. As shown in Fig. 1, each CT absorption spectrum consists of two bands. In the case of **1a**, the longer wavelength band is partially resolved and appears as a shoulder at 497 nm.† The shorter wavelength band has a maximum at 406 nm. When an electron-donating substituent, a methyl or a methoxy group, is introduced on the benzene ring, the first band is significantly red-shifted and the two bands become well resolved. Naphthylcyclopropanes also exhibited two resolved CT bands. In order to make comparisons, we also measured the

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† For **1a**, the first CT absorption maximum (497 nm) was determined by gaussian deconvolution of the spectrum replotted against wavenumber.

**Table 1** Oxidation potentials ($E_{ox}$)[a] and ionization potentials ($E_i$)[b] of arylcyclopropanes and the related arene donors, and the CT absorption maxima ($\lambda_{max}$ and $h\nu_{CT}$) of their EDA complexes with TCNE in methylene chloride[c]

| Donor | $E_{ox}$/V *vs.* SCE | $\lambda_{max}$/nm | $E_i$[d]/eV | $h\nu_{CT1}$/eV | $h\nu_{CT2}$/eV |
|---|---|---|---|---|---|
| **1a** | 1.78 | 497, 406 | 8.61, 912 | 2.49 | 3.05 |
| **1b** | 1.60 | 524, 412 | (8.27, 8.91) | 2.37 | 3.01 |
| **1c** | 1.35 | 600, 394 | 8.05, 9.08 | 2.07 | 3.15 |
| **1d** | 1.47 | 598, 438 | (7.94, 8.70) | 2.07 | 2.83 |
| **1e** | 1.49 | 598, 474 | (7.94, 8.48) | 2.07 | 2.61 |
| **2a** | 1.74 | 472s, 404 | (8.57, 9.00) | 2.64 | 3.07 |
| **2b** | 1.36 | 582, 396 | (8.01, 9.01) | 2.13 | 3.13 |
| Benzene | 2.6 | 390 | 9.23 | 3.18 | — |
| Toluene | 2.15 | 414 | 8.85, 9.34 | 2.99 | — |
| Cumene | 2.29 | 404 | 8.98, 9.21 | 3.07 | — |
| *p*-Xylene | 1.90 | 468s, 418 | 8.43, 9.14 | 2.65 | 2.97 |
| 4-(Isopropyl)toluene | 1.99 | 476s, 422 | | 2.60 | 2.94 |
| Anisole | 1.70 | 512, 388 | 8.39, 9.22 | 2.42 | 3.19 |
| *p*-Methylanisole | 1.56 | 562, 396 | 8.18, 9.11 | 2.21 | 3.13 |
| 4-(Isopropyl)anisole | 1.53 | 558, 398 | | 2.22 | 3.11 |
| Naphthalene | 1.66 | 550, 428 | 8.15, 8.88 | 2.25 | 2.90 |
| 1-Methylnaphthalene | 1.62 | 580, 452 | 7.95, 8.74 | 2.14 | 2.74 |
| 2-Methylnaphthalene | 1.60 | 578, 458 | 7.93, 8.63 | 2.14 | 2.71 |
| Diphenylmethane | 2.11 | 406 | | 3.05 | — |
| 2,2-Diphenylpropane | 2.13 | 408 | | 3.04 | — |
| Di-*p*-anisylmethane | 1.60 | 564, 394 | | 2.20 | 3.15 |

[a] Measured in acetonitrile by cyclic voltammetry. SCE = Standard calomel electrode. [b] From refs. 22 and 23. [c] [Donor] = [TCNE] = $2.5 \times 10^{-2}$ mol dm$^{-3}$. [d] Values in parentheses are estimated from the relation: $h\nu_{CT1} = 0.902\ E_i - 5.09$.

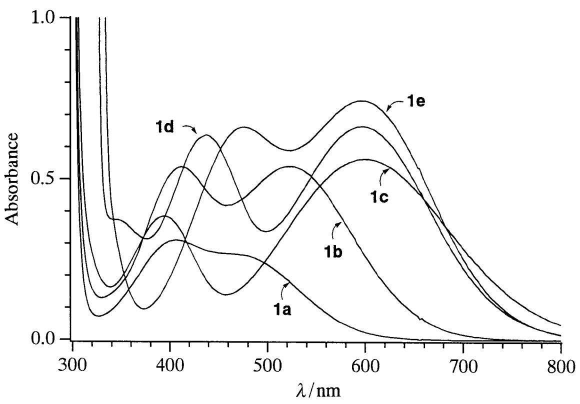

**Fig. 1** The CT absorption spectra of the EDA complexes of **1** ($2.5 \times 10^{-2}$ mol dm$^{-3}$) with TCNE ($2.5 \times 10^{-2}$ mol dm$^{-3}$) in methylene chloride

CT absorption spectra of the TCNE EDA complexes of arene donors related to **1**–**2** and the results are summarized in Table 1.

The observation of bathochromic shifts in the CT absorption maxima with increasing electron-donating ability of the donors is in accord with Mulliken theory.[20] For weak EDA complexes with a common acceptor, the energy of the CT transition ($h\nu_{CT}$) correlates to the ionization potentials ($E_i$) of the donors: $h\nu_{CT} = E_i - E_A - \omega$, where $E_A$ is the electron affinity of the acceptor and $\omega$ is the electrostatic work term. While $E_i$ values of many arenes are known (Table 1),[22] those of arylcyclopropanes are reported only for **1a**[23a,c] and **1c**.[23a] Nevertheless, a plot of $h\nu_{CT1}$ against $E_i$ for the TCNE complexes of **1a**, **1c** and the arenes is linear and expressed as: $h\nu_{CT1} = 0.902E_i - 5.09$ ($r^2 = 0.953$). The first $E_i$ values for **1b**, **1d**, **1e**, **2a** and **2b** are estimated according to the relation with the observed CT transition energies ($h\nu_{CT1}$) and presented in parentheses in Table 1. The second $E_i$ values in parentheses are based on the difference between the $h\nu_{CT1}$ and $h\nu_{CT2}$ values of the donors.

CA and 1,2,4,5-tetracyanobenzene (TCNB) were also used as acceptors to investigate the EDA behaviour of these arylcyclopropanes. Since they are weaker acceptors than TCNE, only tailing CT absorptions were observed with phenyl- and *p*-tolylcyclopropanes **1a**, **1b** and **2a**. With naphthyl- and *p*-anisyl-derivatives, distinct CT absorption maxima were observed (Table 2). Again, the absorption maxima are red-shifted compared to those of the parent arenes or alkyl arenes. In the combination of **1e**–TCNB, a yellow solid was obtained. The IR spectrum is essentially identical to the superposition of the spectrum of each component and the result of the elemental analysis is consistent with the 1:1 complex.‡

### CT excitation of the EDA complexes of 1 and 2

Photoexcitation of the EDA complexes in methylene chloride solutions was carried out by using a 2 kW xenon lamp with a water IR-filter and a glass filter. Despite the intense CT absorption bands, the TCNE complexes of **1** and **2** failed to undergo chemical reaction. Thus, even after 10 h of irradiation ($\lambda > 390$ nm), the cyclopropanes remained intact. Similarly, no reaction was observed with the CA EDA complexes of **1** or **2b**. In the case of diphenylcyclopropane **2a**, however, inefficient photoreaction took place. Irradiation ($\lambda > 505$ nm) of a 5 cm$^3$ methylene chloride solution containing **2a** (1.20 mmol) and CA (0.10 mmol) for 6 h resulted in the formation of addition product **3** in 0.6% yield with recovery of **2a** (96%).

### Picosecond absorption spectroscopy of the EDA complexes of 1a and 2a

It is conceivable that the lack of chemical change in the photoirradiation of the **1**– and **2**–TCNE complexes is due to fast back electron transfer (large $k_{bet}$) of the photogenerated ion–radical pairs. In order to address this point, we undertook picosecond time-resolved spectroscopic measurements with the **1a**– and **2a**–TCNE complexes. Fig. 2(*a*) and (*b*) show the transient absorption spectra obtained by pulsed 355 nm excitation of these complexes in cyclohexane with a mode-locked Nd$^{3+}$:YAG laser.§ For the **1a**–TCNE complex, excitation with a 25 ps pulse resulted in immediate production of transient absorption bands near 450 and 560 nm. These bands decayed within *ca.* 70 ps. Excitation of the **2a**–TCNE complex afforded similar transient absorption spectra which also decayed within *ca.* 70 ps. We assign the band near 450 nm to TCNE anion radical (TCNE$^{\bullet -}$) and that at *ca.* 550 nm to cation radicals **1a**$^{\bullet +}$ and

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‡ It would be desirable to investigate the molecular arrangement of the EDA complex. However we have not yet accomplished the X-ray analysis.

§ In methylene chloride no transient absorption was observed, which indicates that the lifetimes of ion radical pairs [**1a**$^{\bullet +}$, TCNE$^{\bullet -}$] and [**2a**$^{\bullet +}$, TCNE$^{\bullet -}$] are much shorter than 25 ps.

**Table 2** CT absorption maxima of the EDA complexes of arylcyclopropane and arene donors with CA or TCNB in methylene chloride[a]

| | CA | | TCNB | |
|---|---|---|---|---|
| Donor–acceptor | $\lambda_{max}$/nm | $h\nu_{CT}$/eV | $\lambda_{max}$/nm | $h\nu_{CT}$/eV |
| **1c** | 522 | 2.37 | 424 | 2.92 |
| **1d** | 522 | 2.37 | 428 | 2.90 |
| **1e** | 504 | 2.46 | 426 | 2.91 |
| **2b** | 500 | 2.48 | 400sh | 3.10 |
| Anisole | 432 | 2.87 | 372sh | 3.33 |
| *p*-Methylanisole | 504 | 2.48 | 402 | 3.08 |
| 4-(Isopropyl)anisole | 492 | 2.52 | 396 | 3.13 |
| Naphthalene | 476 | 2.60 | 400 | 3.10 |
| 1-Methylnaphthalene | 504 | 2.46 | 418 | 2.97 |
| 2-Methylnaphthalene | 500 | 2.48 | 416 | 2.98 |
| Di-*p*-anisylmethane | 500 | 2.48 | 400 | 3.10 |

[a] Absorption spectra were measured with $2.0 \times 10^{-2}$ mol dm$^{-3}$ of CA or TCNB and *ca.* $5 \times 10^{-2}$ mol dm$^{-3}$ of a donor.

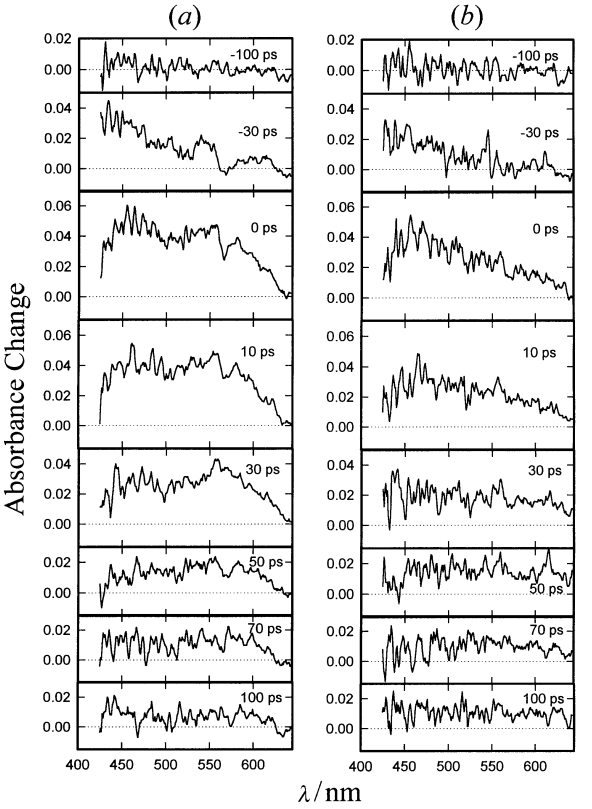


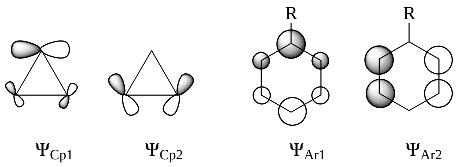
**Fig. 2** Difference absorption spectra as a function of time after excitation with a 355 nm, 25 ps pulse, measured for (*a*) the **1a**–TCNE EDA complex and (*b*) the **2a**–TCNE EDA complex in cyclohexane at 23 °C

**2a**$^{\bullet+}$. These assignments are supported by the observations that electrochemically generated TCNE$^{\bullet-}$ has its absorption maximum at 435 nm[21a,b] in methylene chloride and that **1a**$^{\bullet+}$ generated by photoinduced electron transfer[15f,g,24] or pulse radiolysis[25] exhibits broad absorption whose maximum is in the range of 540–550 nm. The absorption maximum of **2a**$^{\bullet+}$ has been observed at 520 nm.[24]

## Discussion

It is well known that TCNE and CA form EDA complexes with arenes and other electron donors. The CT absorptions of such EDA complexes are generally due to electronic transitions from the high-lying molecular orbitals of the donors to the lowest unoccupied molecular orbitals (LUMOs) of the acceptors. Arylcyclopropanes **1** and **2** also form EDA complexes with TCNE and CA. It is important to note that the arylcyclopropane EDA complexes exhibit lower energy CT absorptions relative to the corresponding arenes. For example, the **1a**–TCNE complex can be compared with the TCNE complexes of benzene ($\lambda_{max}$ 390 nm), toluene ($\lambda_{max}$ 414 nm) or cumene ($\lambda_{max}$ 404 nm). While the CT absorption spectra of these arenes possess apparently single bands, the CT absorption of the **1a**–TCNE complex appear as two partially resolved bands, with the first CT band significantly red-shifted ($\lambda_{max}$ 497 nm, $h\nu_{CT1}$ 2.49 eV). The other arylcyclopropane–TCNE complexes also show similar features in their CT absorption spectra. These observations indicate that the highest occupied molecular orbitals (HOMOs) of **1** and **2** are energetically destabilized relative to their next (N) HOMOs or the HOMOs of the corresponding arenes. Conjugative interaction between a cyclopropyl and adjacent n and π systems is a well-documented phenomenon.[23,26–29] In addition to a cyclopropyl group, other strained hydrocarbon skeletons[30] act as electron-donating groups. An interpretation for such electron-donating effect of a cyclopropyl group can be made by the perturbation molecular orbital (MO) theory.

A qualitative MO picture for an arylcyclopropane is obtained by fragment interaction between a cyclopropane and a benzenoid ring. One of the degenerate HOMOs of cyclopropane[31,32] is antisymmetric ($\Psi_{Cp1}$). It is antibonding between two carbons but has bonding character between either of these and the third one. The other HOMO is symmetric with bonding character between a pair of carbons ($\Psi_{Cp2}$). The HOMO and NHOMO of an arene are $\Psi_{Ar1}$ and $\Psi_{Ar2}$ orbitals. Antibonding interaction between $\Psi_{Cp1}$ and $\Psi_{Ar1}$ orbital would lead to the HOMO of an arylcyclopropane. The resulting HOMO has mixed π ($\Psi_{Ar1}$) and σ ($\Psi_{Cp1}$) character and is higher in energy than $\Psi_{Ar1}$ owing to mixing of $\Psi_{Cp1}$ into $\Psi_{Ar1}$. The NHOMO of an arylcyclopropane may be derived from $\Psi_{Ar2}$ with little interaction with $\Psi_{Cp1}$ or $\Psi_{Cp2}$.



Removal of one electron from the arylcyclopropane HOMO of partial σ-character would result in the corresponding cation radical whose spin and charge is delocalized into the cyclopropane ring. Thus two of the σ-bonds, C1–C2 and C1–C3, are expected to be weakened. Indeed, evidence accumulated to date reveals that the ring bonds of cation radicals **1a**$^{\bullet+}$ and **2a**$^{\bullet+}$ are weakened and susceptible to nucleophile-assisted ring cleavage.[¶,15,24] However, the present results show that cyclopro-

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¶ It is not yet known whether phenylcyclopropane cation radical has a stationary structure with two elongated ring bonds or with one lengthened ring bond. For parent cyclopropane cation radical, an equilibrium structure with one lengthened bond is accepted as the lowest energy species.[2] Vinylcyclopropane cation radical in a particular conformation is shown to have a structure with two elongated ring bonds by *ab initio* STO-3G calculations.[33]

panes **1** and **2** undergo no net reaction following CT excitation with TCNE though ET from the donors to TCNE does occur. Clearly, the lifetimes of the resulting ion-radical pairs are too short to undergo any chemical transformation. We evaluate the lifetimes of the ion-radical pairs [**1a**$^{\bullet+}$, TCNE$^{\bullet-}$] and [**2a**$^{\bullet+}$, TCNE$^{\bullet-}$] to be *ca.* 30 ps in cyclohexane. For the CA complexes, net chemical reaction is observed only in the CT excitation of the **2a**–CA complex though the efficiency is very low. It is conceivable that cation radical **2a**$^{\bullet+}$ in the photogenerated ion-radical pair undergoes the C1–C2 (or C3) ring cleavage which is nucleophilically assisted by the paired anion radical CA$^{\bullet-}$. Intramolecular hydrogen transfer in the resulting intermediate **4** leads to the formation of **3**. On the other hand, similar CT excitation of the **1**–CA or **2b**–CA complexes ends up with no reaction.

It appears that at least two factors are concerned with the reactivity of **1** and **2** upon their CT excitation. First, of course, is the lifetime of the photogenerated ion-radical pairs. Ion-radical pairs derived from stronger electron acceptors or more electron-donating arylcyclopropanes are expected to have shorter lifetimes because they are considered to be in the Marcus inverted region for the back electron transfer.[21*c–e*] In other words, ion-radical pairs with less negative free energy change for back electron transfer are expected to have larger $k_{\mathrm{bet}}$ values. Although the lifetime of the ion-radical pair [**2a**$^{\bullet+}$, CA$^{\bullet-}$] has not yet been measured, a longer lifetime to undergo chemical change may be expected since the ion-radical pair is higher in energy than the [**2a**$^{\bullet+}$, TCNE$^{\bullet-}$] ion-radical pair. By the same token, the lifetime of the ion-radical pair [**2a**$^{\bullet+}$, CA$^{\bullet-}$] is probably longer than the ion-radical pair [**2b**$^{\bullet+}$, CA$^{\bullet-}$].

A second factor is the inherent reactivity of **1**$^{\bullet+}$ and **2**$^{\bullet+}$, which is related to the weakness of their C1–C2 (C3) σ-bonds relative to susceptibility toward nucleophiles. Apparently, the cation radical reactivity is affected by substituents. Diphenyl derivative **2a**$^{\bullet+}$ is more reactive than monophenyl **1a**$^{\bullet+}$. This is probably due to steric effects. The two phenyl groups in **2a**$^{\bullet+}$ repulsively interact with each other and with the C2- and C3-methylenes, which would make the σ-bonds of **2a**$^{\bullet+}$ weaker compared to those of **1a**$^{\bullet+}$. Electronic effects of substituents are also important. As the electron-donating ability of the aryl moiety becomes higher the reactivity of the cyclopropane donors seems to decrease. The weakness of the cation radical C1–C2 (C3) bonds is related to σ-character in the arylcyclopropane HOMO. Based on the fragment interaction as discussed above, the HOMOs of **1b**–**e** and **2b** are expected to have less appreciable σ-character compared with those of **1a** and **2a**. Accordingly, the reactivity of **1b**$^{\bullet+}$–**e**$^{\bullet+}$ or **2b**$^{\bullet+}$ should be lower since their C1–C2 (C3) σ-bonds are expected to be stronger than those of **1a**$^{\bullet+}$ or **2a**$^{\bullet+}$.

Bathochromic shifts in the first CT absorption maximum ($h\nu_{\mathrm{CT1}}$) for arylcyclopropane donors relative to the corresponding arenes reflect the degree of HOMO destabilization due to mixing of $\Psi_{\mathrm{Cp1}}$ into $\Psi_{\mathrm{Ar1}}$ orbitals. Since the degree of σ-character in the arylcyclopropane HOMO is correlated with the degree of HOMO destabilization, inspection of the CT absorption spectra for **1** and **2** provides a qualitative measure for their reactivity in the cation radical manifold. For example, the CT absorption maxima ($h\nu_{\mathrm{CT1}}$) of **1a** and **1b** are red-shifted by 0.69 and 0.62 eV relative to those of benzene and toluene, respectively. On the other hand, the corresponding red-shifts of **1c**–**e** are smaller: 0.35, 0.18 and 0.18 eV, respectively, relative to those of anisole for **1c** and naphthalene for **1d** and **1e**. A similar trend is observed for the diarylcyclopropanes. The first CT absorption maximum of **2a** is red-shifted by *ca.* 0.40 eV relative to diphenylmethane whereas that of **2b**, a much less reactive donor, is red-shifted by only *ca.* 0.07 eV compared to dianisylmethane.

Although qualitative, the reactivity index based on the observed spectral trend is also consistent with previous experimental results. Recently, Mazzocchi and co-workers studied ET photoreactions of arylcyclopropanes with phthalimides.[13*a,d*] They reported that **1a** and **1b** were reactive to give cycloadducts but **1c** was not. It was suggested that the positive charge of **1c**$^{\bullet+}$ resides predominantly on the oxygen, making nucleophilic attack by phthalimide anion radical on the cyclopropane moiety less likely. Recently, the reactivity of **1**$^{\bullet+}$ and **2**$^{\bullet+}$ toward alcohols has been investigated by using laser flash photolysis technique.[15*f,g*,24] The rate constants ($k_{\mathrm{add}}$) for nucleophilic ring cleavage of arylcyclopropane cation radicals by methanol decrease with increasing electron-donating ability of the aryl group. The $k_{\mathrm{add}}$ values are $1.1 \times 10^7$ and $3.3 \times 10^5$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 25 °C for **1a**$^{\bullet+}$ and **1b**$^{\bullet+}$, respectively. On the other hand, the $k_{\mathrm{add}}$ value for **1c**$^{\bullet+}$ is immeasurably low, much lower than $10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$. For the diarylcyclopropanes, the $k_{\mathrm{add}}$ value[15*g*] for **2a**$^{\bullet+}$ is reported to be $1.7 \times 10^7$ dm$^3$ mol$^{-1}$ s$^{-1}$ whereas that of **2b**$^{\bullet+}$ is $2.7 \times 10^4$ dm$^3$ mol$^{-1}$ s$^{-1}$.[24]

## Conclusions

Photoexcitation of the EDA complexes derived from the arylcyclopropane donors and TCNE generates an excited state that is well described in terms of a singlet ion-radical pair. The lifetime is generally too short to undergo any other chemical reactions before back electron transfer occurs. In the case of the CA complexes, net chemical change is observed only for the CT excitation of the **2a**–CA complex although the efficiency is very low. It appears that at least two factors are concerned with the reactivity of **1** and **2** following CT excitation. First is the lifetime of the photogenerated ion-radical pairs. Second is the inherent reactivity of **1**$^{\bullet+}$ and **2**$^{\bullet+}$, which is related to the weakness of their C1–C2 (C3) σ-bonds relative to susceptibility toward nucleophiles. Substituent effects play a decisive role in the reactivity of arylcyclopropane cation radicals. A qualitative measure of the electronic effects of substituents on the reactivity of **1**$^{\bullet+}$ and **2**$^{\bullet+}$ can be obtained from considerations of the CT absorption spectra for **1** and **2**.

## Experimental

### General methods

Melting points were measured on a Yamato MP-21 apparatus and are uncorrected. A Shimadzu IR-435 spectrometer, a Hewlett-Packard HP 8452 diode array spectrophotometer, Hitachi M-2500S spectrometer and a Varian XL-200 spectrometer were used for measurements of IR, UV–VIS, MS and NMR spectra (*J* values in Hz), respectively. $^1$H NMR (200 MHz) chemical shifts are reported in ppm downfield from SiMe$_4$ internal standard. $^{13}$C NMR (50 MHz) chemical shifts in ppm are based on CDCl$_3$ resonance (77.00 ppm). Cyclic voltammetric measurements were carried out in acetonitrile with 0.1 M tetraethylammonium perchlorate as a supporting electrolyte and SCE as a reference electrode by using a Yanagimoto P-1000 voltammetric analyser equipped with a function generator.

### Materials

TCNE was purchased and purified by repeated sublimation. Extra pure grade CA and TCNB were purchased and used as received. Commercially available spectroscopic grade solvents were distilled over calcium hydride prior to use. Cyclopropanes **1** and **2** were synthesized by the addition of dibromocarbene[34*a,b*] to arylethylenes followed by reduction with Bu$_3$SnCl–LiAlH$_4$.[34*c*]

### Picosecond absorption spectroscopy

The modified Quantel/Continuum Nd:YAG laser system used to record the transient absorption spectra was described previously.[35] A cyclohexane solution of **1a** (0.4 mol dm$^{-3}$) with TCNE (10 mmol dm$^{-3}$) or of **2a** (0.2 mol dm$^{-3}$) with TCNE (5 mmol dm$^{-3}$) in a 5 mm pathlength cell was excited by pulses having a half-width of *ca.* 25 ps at 355 nm which were generated from the 1064 nm fundamental by the use of harmonic generating crystals. The energies of the excitation pulses were measured by diverting *ca.* 10% of each pulse into the probe (Model RjP-735) of an energy meter (Laser Precision Corp. Model Rj-7200) and were in the range of 0.1–0.2 mJ pulse$^{-1}$. The beam diameter at the sample was *ca.* 2 mm. The absorbance change at a selected time after excitation was monitored by means of a 30 ps continuum pulse. This white-light probe pulse was generated when the sufficiently energetic portion of the split, original 1064 nm pulse was focused into a 20 cm cell that contained a 1:1 $H_2O$–$D_2O$ mixture. The probe pulse was split and directed into the sample cell and the reference cell. After transmission through these cells, the probe pulses were focused at the slit of a 0.32 m spectrograph (Instruments SA Model HR-320). The spectrograph output was imaged onto an EG&G Princeton Applied Research (PAR) two-dimensional silicon intensified target detector (Model 1254E) coupled to a PAR 1216 multichannel detector controller. This detector was interfaced with an IBM microcomputer that controlled the necessary optical hardware and electronics during data acquisition, processed the data, and presented the data graphically. To improve the signal-to-noise ratio, each difference absorption spectrum is the result of averaging data from at least 400 excitation laser pulses. The difference absorption spectrum spans a wavelength range from approximately 425 to 650 nm.

### Isolation of the 1e–TCNB complex

To a hot solution of TCNB (20 mg, 0.10 mmol) in 20 cm$^3$ of methanol was added 23 mg (0.14 mmol) of **1e** in 1 cm$^3$ of methanol. The mixture was allowed to stand in the open air in the dark at room temp. Slow evaporation of the solvent over a period of 2 d yielded 9 mg of yellow needles; mp 228 °C. Found: C, 79.61; H, 3.90; N, 16.35%. $C_{25}H_{14}N_4$ (as 1:1 complex) requires C, 79.75; H, 4.07; N, 16.18%. $\nu_{max}$(KBr)/cm$^{-1}$ 3100, 3045, 3000, 2235 (CN ), 1630, 1598, 1507, 1488, 1276, 1033, 1020, 952, 920, 910, 853, 821, 760, 503, 476. $\delta_H$(200 MHz, CDCl$_3$) 0.81 (2 H, m), 1.02 (2 H, m), 2.06 (1 H, m), 7.19 (1 H, dd, *J* 8.6, 2.0), 7.40 (2 H, m), 7.53 (1 H, br d, *J* 1.5), 7.75 (3 H, m), 8.25 (2 H, s).

### CT excitation of the EDA complexes of 1 or 2 with TCNE

Typically, a 5 cm$^3$ methylene chloride solution containing **1** or **2** (0.25 mmol) and TCNE (0.25 mmol) in a Pyrex test tube was irradiated for 10 h at 19 °C by using a 2 kW xenon lamp through a water IR-filter and a glass filter (Toshiba L-42, $\lambda > 390$ nm). Then the solvent was evaporated and the remaining material was analysed by $^1$H NMR with 1,1,1,2-tetrachloroethane (4.27 ppm in CDCl$_3$) or 1,1,2,2-tetrachloroethane (5.92 ppm in CDCl$_3$) as an internal standard. No photoproduct was observed in any case but the cyclopropanes were recovered in >98% yield. Similar photoreactions of **1** and **2** in cyclohexane also ended up with recovery of the starting material.

### CT excitation of the EDA complexes of 1 or 2 with CA

Typically a 5 cm$^3$ methylene chloride solution containing **1** or **2** (1.20 mmol) and CA (0.10 mmol) in a Pyrex test tube was irradiated as described above. In this case, a Toshiba Y-52 glass filter ($\lambda > 505$ nm) was used instead of L-42. Analysis of the reaction mixture by $^1$H NMR showed no reaction occurred for **1** and **2b** and they were recovered in >98% yield. In the case of **2a**, the NMR analysis indicated the presence of a photoproduct with recovery of **2a** in 96%. The reaction mixture was triturated with diethyl ether and unreacted CA (22 mg, 0.09 mmol, 90%) was removed by filtration. The filtrate was concentrated and subjected to silica gel TLC. Development with methylene chloride afforded 179 mg (0.92 mmol, 92%) of recovered **2a** ($R_f = 0.99$) and 3 mg (0.01 mmol, 0.6%) of **3** ($R_f = 0.30$). 1-(3,3-Diphenylprop-2-enyloxy)-4-hydroxy-2,3,5,6-tetrachlorobenzene (**3**), mp 139.5–143 °C (decomp., from $CH_2Cl_2$–hexane). $\nu_{max}$(KBr)/cm$^{-1}$ 3462 (OH), 1492, 1438, 1390, 1373, 1316, 1268, 1182, 1030, 947, 761 and 701. $\delta_H$(200 MHz, CDCl$_3$) 4.61 (2 H, d, *J* 7.2), 5.81 (1 H, br s), 6.45 (1 H, t, *J* 7.2), 7.11 (2 H, m), 7.29 (4 H, m), 7.34 (4 H, m). $\delta_C$(50 MHz, CDCl$_3$) 71.40 (1 C, −CH$_2$–O−), 118.75 (2C, C-2,6), 122.41 (1 C, =CH−), 127.64 (2 C, C-3,5), 127.69 (2 C, phenyl *ortho*), 127.74 (1 C, phenyl *para*), 127.96 (1 C, phenyl *para*), 128.18 (2 C, phenyl *meta*), 128.22 (2 C, phenyl *ortho*), 129.67 (C, phenyl *meta*), 138.48 (1 C, phenyl *ipso*), 141.28 (1 C, phenyl *ipso*), 146.00 (1 C, Ph$_2$=C=), 146.17 (1 C, C-4), 147.15 (1 C, C-1). *m/z* 442 (M$^+$ + 4, 0.03%), 441 (M$^+$ + 3, 0.02), 440 (M$^+$ + 2, 0.07), 439 (M$^+$ + 1, 0.03), 438 (M$^+$, 0.05), 404 (0.7), 248 (12), 246 (18), 194 (21), 193 (100), 178 (16). HRMS: calc. for $C_{21}H_{14}O_2Cl_4$: 437.9748; Found: 437.9773. It was found that **3** could be independently synthesized from 1,1-diphenylpropene and CA. Irradiation of 1,1-diphenylpropene (39 mg, 0.20 mmol) and CA (49.5 mg, 0.20 mmol) in 10 cm$^3$ methylene chloride with shorter wavelength light (CA excitation, $\lambda > 370$ nm) for 2 h afforded **3** (24 mg, 27%).

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