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SHORT COMMUNICATION

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Photochromism of Acetyl-Cyclophanochromene: Intriguing Stabilization of Photogenerated Colored *o*-Quinonoid Intermediates

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The photochromism of a chromene annulated on [2.2]paracyclophane, Ac-CPC, was investigated. Whereas the parent chromene 2,2-diphenylbenzopyran shows photoinduced coloration only at very low temperatures, acetyl-cyclophanochromene Ac-CPC was found to exhibit room-temperature photochromism. With no extended conjugation due to absence of any substituents in two cofacially-oriented aryl rings, the through-space delocalization of π-electrons, i.e., the phane effect, manifests nicely leading to the stabilization of the photogenerated colored o-quinonoid intermediates. The interaction between cofacial aryl rings is supported by the distance between them, as revealed by X-ray crystal structure analysis. Additionally, electrophile···nucleophile interactions are surmised to be important for intriguingly longer persistence of the photogenerated intermediates of Ac-CPC relative to the lifetime of the photogenerated intermediate generated from the parent cyclophanochromene, which is devoid of an electron-withdrawing acetyl group.

Introduction

The demand for functional materials is on the rise.[1] A profound obsession for functional materials is reflected from explosive research on solar cells, optoelectronic materials, sensors, biomaterials, data storage devices, and so on.[2] Organic photochromic molecules are a class of functional materials that have been extensively used in a variety of applications, for instance, in UV-protective laser goggles, ophthalmic lenses, display systems, variable transmission glasses, information recording and storage devices, optical switches, and nonlinear device components.[2e,2f,3,4] The phenomenon of reversible interconversion of a substance between two physically and chemically distinct states by the influence of light and heat is known as photochromism.[3] 2,2-Diarylbenzopyrans – popularly known as chromenes – are important members of the family of organic photochromic molecules.[3] Chromenes undergo C–O bond heterolysis in the presence of UV light to give rise to colored reactive open forms, termed *o*-quinonoid intermediates. The latter can be reverted back to their original colorless closed forms by the influence of visible light or by action of heat.[5] Modulation of the spectrokinetic properties of the colored intermediates derived from chromenes has been thoroughly investigated by one of us.[6–11] We explored the influence of electronic effects in a series of substituted 2,2-diarylbenzopyrans.[6] Aromatic annulation, electronic effects transmitted by arylation, and toroidal conjugation extant to hexaphenylbenzenes have been shown to influence the photochromic phenomena.[7,8] In a novel series of helical chromenes, helicity – as a steric force – has been shown to guide the persistence of the photogenerated colored intermediates.[9] The influence of through-space electronic effects has also been demonstrated in chromenes that contain cofacially oriented aryl rings based on 1,8-diarylnaphthalene[10] and in paracyclophanes grafted with chromenes (i.e., cyclophanochromenes, CPCs).[11] In continuation of ongoing investigations on CPCs, we examined the intriguing photochromic behavior observed for a novel chromene, that is, acetyl-cyclophanochromene (Ac-CPC, Figure 1).

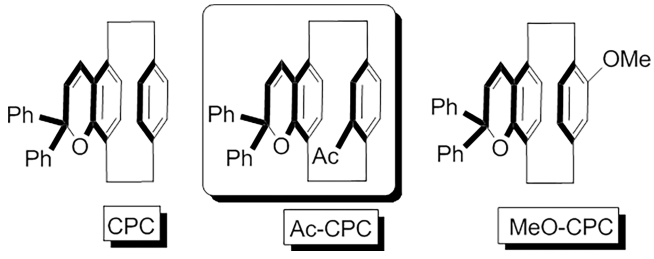

Figure 1. Molecular structures of CPC, Ac-CPC, and MeO-CPC.

[2.2]Paracyclophane is a widely used scaffold that has been exploited in the development of sensors,[12] asymmetric catalysts,[13] organic light-emitting diodes,[14] and solar cells.[14] For the first time, we exploited this novel scaffold to demonstrate the phane effect on the photochromic phenomenon.[11] During these investigations, we found that the new acetylated derivative, Ac-CPC, also exhibits photochromism at ambient temperatures, which is not observed

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for the parent chromene, that is, 2,2-diphenylbenzopyran; the latter shows photocoloration only at very low temperatures (173–263 K).[15] We herein report that photoexcitation of Ac-CPC leads to colored *o*-quinonoid intermediates that are intriguingly more stable than those derived from the parent CPC; indeed, persistence of the colored intermediates is comparable to that of the methoxy-substituted cyclophanochromene (MeO-CPC, Figure 1). Besides the phane effect, electrophile···nucleophile interactions are additionally surmised to be responsible for the increased persistence of the colored *o*-quinonoid intermediate(s) of Ac-CPC.

Results and Discussion

Synthesis of Cyclophanochromene Ac-CPC

The synthetic methodology employed for the preparation of Ac-CPC is depicted in Scheme 1. Commercially available [2.2]paracyclophane was acetylated with acetyl chloride/$AlCl_3$ in dry CH_2Cl_2. Formylation of the product with $CHCl_2OCH_3/TiCl_4$ followed by Dakin oxidation led to the corresponding phenol. This phenol was annulated with 1,1-diphenylpropargyl alcohol by using PPTS (pyridinium *p*-toluenesulfonate) as a catalyst to afford Ac-CPC, which was thoroughly characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopic data and ESI mass spectrometry. The structure of Ac-CPC was unequivocally established by single-crystal X-ray structure determination (Figure 2).

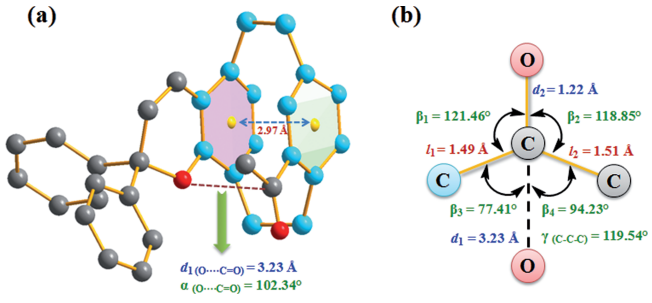


Figure 2. (a) Perspective drawing of the X-ray-determined molecular structure of Ac-CPC; hydrogen atoms are omitted for clarity. Notice the cofacial orientation of the two aryl rings and the proximity of the pyran oxygen atom to the carbonyl carbon atom. (b) Geometrical parameters for the approach of the pyran oxygen atom to the acetyl carbonyl carbon atom, as reported by Dunitz and coworkers (see below).

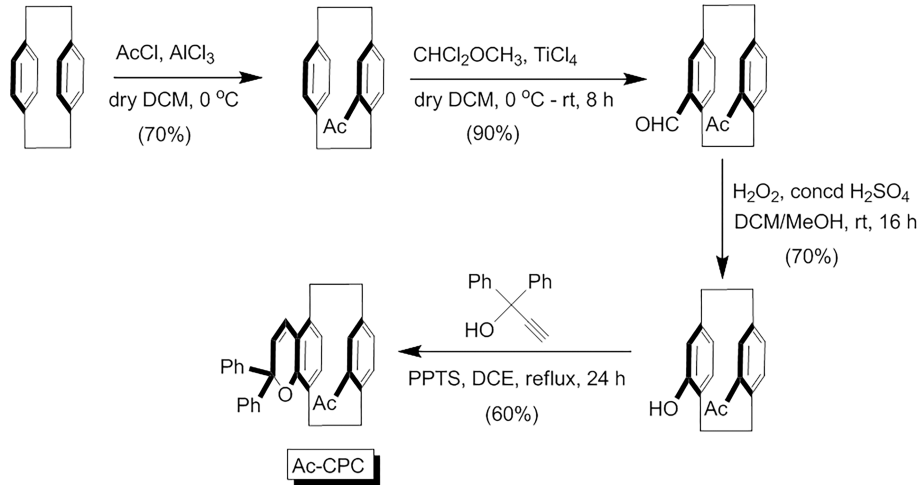
X-ray Single-Crystal Structure Determination of Ac-CPC and Structural Analysis

To examine the relative orientations of the two aryl rings, we undertook crystal structure determination of cyclophanochromene Ac-CPC. Crystals of this compound were readily obtained by slow evaporation of its solution in $CHCl_3/CH_2Cl_2$ at room temperature. X-ray diffraction data collection and subsequent structure determination revealed that the crystals belong to the monoclinic crystal system with the $P2_1/n$ (No. 11) space group. In Figure 2 is shown a perspective drawing of the molecular structure of Ac-CPC. The crystal packing analyses show that the structure is stabilized by weak C–H···O hydrogen bonds.

A closer inspection of the molecular structure in Figure 2 shows that the two aryl rings of the cyclophane are cofacial with a center-to-center distance of 2.97 Å. This distance is lower than the sum of the van der Waals radii of two carbon atoms, which attests to closer interaction between the two cofacially oriented aryl rings. The X-ray-determined structure reveals further that the acetyl functionality and the pyran moiety lie on the same side of the cyclophane. One observes that the pyran oxygen atom approaches the carbonyl carbon atom almost orthogonally, and indeed lies at a distance of 3.23 Å. The angle of approach of the pyran oxygen atom to the carbonyl group turns out to be 102.3° (Figure 2).

Spectrokinetic Behavior of the Photogenerated *o*-Quinonoid Intermediate of Chromene Ac-CPC

The photobehavior of Ac-CPC was examined in toluene (5×10^{-3} M) at 298 K. Upon exposure to UV irradiation (λ_{ex}



Scheme 1. Synthesis of Ac-CPC (DCE = 1,2-dichloroethane).

≈ 350 nm), the colorless toluene solution was found to turn orange-red. The absorption spectra of the solution before and after UV irradiation are shown in Figure 3 along with the observed color changes. Whereas the absorption of Ac-CPC is characterized by a strong shoulder at 336 nm, which tapers off at about 390 nm, that of the photogenerated intermediate is found to exhibit a two-band feature; one observes a relatively sharp band toward the shorter wavelength region with a maximum at 416 nm and another in the longer wavelength region spanning the entire region from 450 to 700 nm (Figure 3). The orange-red color was found to bleach within 2–3 min upon standing in the dark (Figure 3). The decoloration of the colored *o*-quinonoid intermediates was monitored spectrophotometrically at 416 nm. Decay of the colored intermediate, as monitored by a change in the absorption with time, is also shown in Figure 3. The kinetic decay trace was best fitted to a mono-exponential function (Figure 3), which permitted determination of the rate constant for reversion of the colored form to the colorless form. The rate constant thus extracted was 0.011 s^{-1} at 298 K.

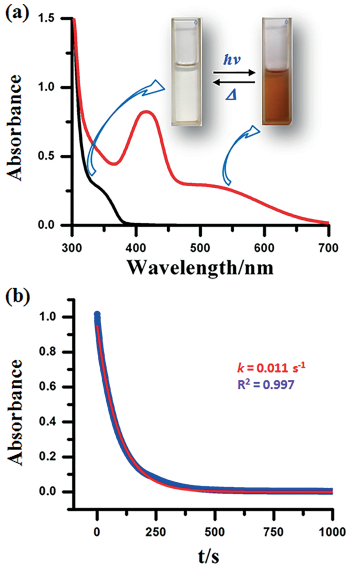
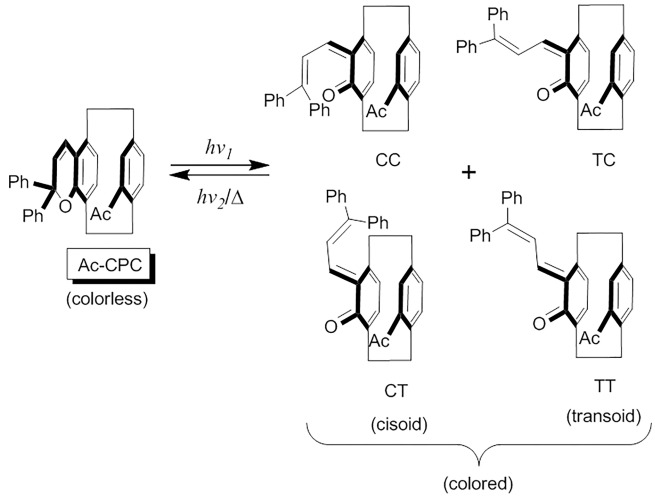


Figure 3. (a) Absorption spectra of Ac-CPC in toluene (5×10^{-3} M) before (black) and after (red) photoirradiation. (b) Decay profile for thermal bleaching of the colored form of Ac-CPC at 298 K in toluene; kinetics were followed by monitoring the change in the absorbance with time at 416 nm at 298 K subsequent to photoexcitation of the colorless solution of Ac-CPC at 350 nm for a brief period.

Stabilization of *o*-Quinonoid Intermediates by a Combination of the Phane Effect and Electrophile···Nucleophile Interactions

Mechanistic investigation of the photochromism of 2,2-diarylbenzopyrans is well documented.[5] Photoirradiation of colorless pyrans (closed form) leads to coloration, and the color is attributed to the formation of open forms, namely, *o*-quinonoid intermediates, derived through heterolysis of the C(sp^3)–O bond in the singlet-excited state; for example, as applied to CPCs in Scheme 2. The colored *o*-quinonoid reactive intermediates, owing to their instability, revert to initial colorless closed forms either by heating or by irradiation with visible light. The parent chromene, that is, 2,2-diphenylbenzopyran, is known to exhibit photochromism only at low temperatures (173–263 K).[15] Reversion of the open forms to the closed form is so fast in this case that it is practically impossible to detect the formation of *o*-quinonoid intermediates at room temperature.[15] In principle, four isomeric *o*-quinonoid intermediates may result upon photolysis of chromenes, as shown in Scheme 2. It has been established from laser flash photolysis investigations that the CC isomer reverts rapidly on the nanosecond to millisecond timescale through thermal 6π conrotatory ring closure.[5] Before its decay to the closed form, the CC isomer may produce the TC isomer by C–C bond rotation. The TT isomer can be generated by a two-photon absorption process from chromene passing through the TC isomer. It has been firmly established that only the TC and TT isomers are the ones that are mainly responsible for the observed coloration upon UV irradiation of chromenes. Population of the CT isomers is believed to be abysmally small because of severe steric crowding, which renders it the least thermodynamically stable. Because of the two-photon requirement, the TT isomer is likely to be formed only minimally upon exposure of the chromene to UV irradiation for short periods of time. At shorter durations of irradiation, it is the TC isomer that is predominantly formed, and the colored species is generally attributed to this isomer. We consider that the TC isomer is responsible for the observed color as a result of photoirradiation of Ac-CPC.



Scheme 2. Photochromism of cyclophanochromene Ac-CPC.

We have shown in our previous investigation that CPC and MeO-CPC also exhibit photochromism, and this was attributed to the phane effect;[11] notably, coloration due to *o*-quinonoid intermediates of the simple 2,2-diphenylbenzopyran was simply not observable at room temperature but only at low temperatures (173–263 K). The photogenerated colored *o*-quinonoid intermediates of CPC and MeO-CPC were found to decay at 298 K with rate constants of about

0.023 and 0.012 s^{-1}, respectively.[11] In stark contrast, the colored intermediate in Ac-CPC was found to revert more slowly (k = 0.011 s^{-1}) than that of CPC and with a rate almost comparable to that of MeO-CPC. This is intriguing in view of the fact that in cofacially oriented systems, one would expect the electron-withdrawing groups to destabilize the electron-deficient *o*-quinonoid intermediates.[10] What is it that stabilizes the intermediate of Ac-CPC in a manner that is counterintuitive?

It is evident that the chromene is electron rich in nature, whereas the open form, that is, the *o*-quinonoid intermediate, is electron deficient. Hence, electron-releasing groups attached to the cofacially oriented arenes can stabilize the *o*-quinonoid forms to the extent that the color is observable at room temperature.[10] Several studies have revealed that there are two distinct types of delocalization of charge density in [2.2]paracyclophanes, namely, chromophore state and phane state.[14,16] The first category relates to delocalization through ethylene C–C bonds, and it is mainly observed in paracyclophanes containing long conjugated substituents. The phane state is attributed to through-space delocalization of electronic charge density between the cofacial aryl rings, and it comes into picture if the rings are properly substituted with simple functional groups.[14,16] The cyclophanochromene Ac-CPC described herein contains simple acetyl group, and the interactions in it can be better described by the phane state. Through-space interactions are indeed supported from the X-ray-determined crystal structure of Ac-CPC. The center-to-center distance between the two aryl rings is as short as 2.97 Å, which is a lot lesser than the sum of the van der Waals' radii of two carbon atoms.

The phane effect stabilizes the *o*-quinonoid intermediates of Ac-CPC to the extent that they are accessible and visible at ambient temperature. As depicted in Figure 3, the colored intermediate of Ac-CPC exhibits absorption in the visible region (400–650 nm) with a decay rate constant of 0.011 s^{-1} at 298 K. However, what is intriguing, as mentioned earlier, is that the persistence of the *o*-quinonoid intermediates of Ac-CPC is longer than that of the intermediates of CPC. As shown in Figure 2, the acetyl group lies in close proximity of the pyran oxygen atom. Indeed, one can readily recognize an electrophile···nucleophile interaction between the pyran oxygen atom and the acetyl carbonyl carbon atom in a fashion akin to that of the approach of a nucleophile toward an electrophilic carbonyl group. Pioneering studies by Bürgi and Dunitz have shown that the approach of a nucleophile toward the electrophilic carbonyl group is directional and occurs along what is termed the "Bürgi–Dunitz trajectory".[17] The geometrical parameters (developed by Bürgi and Dunitz) for the nucleophilic approach of the pyran oxygen atom toward the electrophilic acetyl carbonyl group were calculated from the X-ray-determined molecular structure of Ac-CPC and are shown in Figure 2. Clearly, an additional interaction in the form of an electrophile···nucleophile interaction is operative in the closed form of Ac-CPC besides the cyclophane effect. We believe that a similar scenario will likely operate for the photogenerated *o*-quinonoid intermediates of Ac-CPC as well. As shown in Figure 4, we envision that the carbonyl group of the *o*-quinonoid intermediate may function as a nucleophile toward the acetyl carbonyl carbon atom. Thus, electrophile···nucleophile interactions and the phane effect presumably operate in concert to render the *o*-quinonoid intermediates of Ac-CPC more stable than those derived from CPC and comparable to those derived from MeO-CPC. Lest, the persistence of the *o*-quinonoid intermediate in contrary to the expectation cannot be explained. Although limited to a single substrate, the observed photochromic phenomenon brings out how subtle interactions superposed on the phane effect may lead to counterintuitive manifestations.

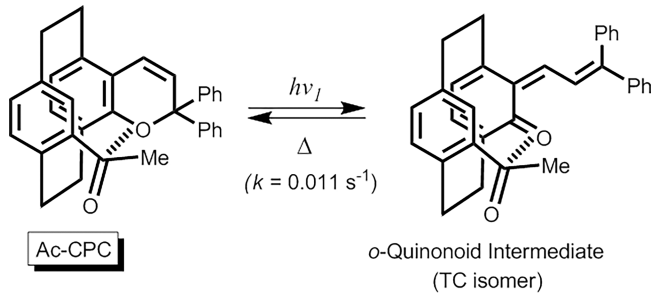


Figure 4. Presumed electrophile···nucleophile interactions in the closed and open forms of Ac-CPC.

Conclusions

The photochromism of [2.2]paracyclophane annulated with 2,2-diphenylpyran, namely, Ac-CPC, was investigated. The photogenerated colored form was found to afford remarkable spectrokinetic properties at room temperature. In contrast to the behavior of the photogenerated intermediates of the parent cyclophane annulated with 2,2-diphenylpyran, that is., CPC, Ac-CPC exhibited coloration at ambient temperatures upon UV irradiation with considerable persistence. The X-ray-determined crystal structure clearly reveals the cofacial arrangement of the two aryl moieties such that the phane effect is amply operative. Additionally, electrophile···nucleophile interactions are surmised to be important for the persistence of the photogenerated *o*-quinonoid intermediates of Ac-CPC in comparison to that of the *o*-quinonoid intermediates generated from the parent cyclophanochromene, that is, CPC, which is devoid of an electron-withdrawing acetyl group.

Experimental Section

General Aspects: 1,2-Dichloroethane was distilled from calcium hydride under an atmosphere of nitrogen prior to use. Anhydrous THF and toluene were freshly distilled from sodium under a nitrogen gas atmosphere. All other solvents were distilled before use. Column chromatography was performed with silica gel of 60–120 μ mesh.

Synthesis of Acetyl-cyclophanochromene (Ac-CPC): 13-Acetyl-4-hydroxy[2.2]paracyclophane (0.20 g, 0.75 mmol), 1,1-diphenylprop-

2-yn-1-ol (0.32 g, 1.50 mmol), and a catalytic amount of PPTS (5 mol-%) were added to dry DCE (10 mL). The mixture was heated at reflux under a nitrogen gas atmosphere for 24 h. After this period, the contents were cooled and washed, and the organic matter was extracted with chloroform (3 × 20 mL). The combined organic extract was dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. After removal of the solvent, the crude mixture was subjected to silica gel column chromatography (4% ethyl acetate in petroleum ether) to obtain pure Ac-CPC, yield 60%. Colorless solid, m.p. 115–117 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54 (d, J = 7.2 Hz, 2 H), 7.40 (t, J = 7.5 Hz, 2 H), 7.21–7.26 (m, 3 H), 6.96–7.09 (m, 4 H), 6.72 (d, J = 7.8 Hz, 1 H), 6.67 (d, J = 9.5 Hz, 1 H), 6.57 (d, J = 7.5 Hz, 1 H), 6.42 (d, J = 9.5 Hz, 1 H), 6.38 (d, J = 7.7 Hz, 1 H), 6.11 (d, J = 7.7 Hz, 1 H), 4.46–4.50 (m, 1 H), 3.63–3.69 (m, 1 H), 3.36–3.40 (m, 1 H), 3.20 (t, J = 12.3 Hz, 1 H), 2.85–2.92 (m, 2 H), 2.69–2.77 (m, 2 H), 2.10 ppm (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.1, 28.1, 31.7, 33.8, 34.8, 80.4, 122.8, 122.9, 124.9, 125.7, 126.1, 126.5, 126.8, 127.4, 127.5, 127.9, 128.1, 128.8, 132.8, 134.0, 135.5, 135.9, 136.0, 137.5, 142.6, 144.3, 144.5, 151.2, 198.6 ppm. IR (KBr): $\tilde{\nu}$ = 3027, 2856, 1662, 1580, 1550, 1491, 1453 cm^{-1}. MS (ESI+): calcd. for $C_{33}H_{28}O_2$ [M + H] 457.2168; found 457.2162.

X-ray Single-Crystal Structure Determination of Ac-CPC: The X-ray diffraction intensity data for crystals of Ac-CPC were collected at 100 K with a Bruker SMART APEX CCD detector system having a Mo-sealed Siemens ceramic diffraction tube (λ = 0.7107 Å) and a highly oriented graphite monochromator operating at 50 kV and 30 mA. The data collection was done in a hemisphere mode and was analyzed with Bruker's SAINTPLUS. The structure was determined by direct methods by using the SHELXL package, and refinement was done by full-matrix least-squares method based on F^2 by using the SHELX-97 program. The hydrogen atoms were largely located from difference Fourier map, and those that could not be identified were fixed geometrically. Hydrogen atoms were refined isotropically and were treated as riding on their non-hydrogen atoms, whereas all non-hydrogen atoms were subjected to anisotropic refinement. Refinement details and other data are given in the Supporting Information.

CCDC-1040065 (for Ac-CPC) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Crystal data and copies of the ^{1}H NMR and ^{13}C NMR spectra of all the compounds.

Acknowledgments

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