## Vicinal-diaryl interactions in stilbenoid hydrocarbons as observed in the through-space charge delocalization of their cation radicals

## **Rajendra Rathore and Jay K. Kochi**

Abstract: The conformational preference of vicinal or 1,2-phenyl groups is probed in two classes of ring-substituted 1,2-diphenylbicyclooctene (stilbenoid) hydrocarbons **1a–1d** and **2a–2c**. UV–vis spectroscopy reveals, and X-ray crystallography verifies, the intramolecular (edge-to-face) orientation for the phenyl–phenyl interaction in stilbenoids **1a–1d**. Most importantly, when two pairs of *ortho*-methyl substituents are present, the cofacial phenyl groups in the stilbenoid donors are established by X-ray crystallography and spectrally observed in the cation radicals (**2a<sup>++</sup>-2c<sup>++</sup>**) by the appearance of new bands with strong absorptions in the near IR with  $\lambda_{max} = 1100-1315$  nm, analogous to those previously observed in intermolecular (aromatic) interactions of aromatic cation radicals.

Key words: stilbenoid hydrocarbon, cation radical, aryl-aryl interaction.

**Résumé** : On a étudié la préférence conformationnelle de groupes phényles vicinaux (ou en positions 1,2) de deux classes d'hydrocarbures, des 1,2-diphénylbicycloocènes (stilbénoïdes) substitués sur le cycle, **1a–1d** et **2a–2c**. La spectro-scopie UV-visible révèle, et la diffraction des rayons X permet de confirmer, l'orientation intramoléculaire (arête vers la face) de l'interaction phényle-phényle dans les stilbénoïdes, **1a-1d**. La diffraction des rayons X a permis d'établir un fait encore plus important, à savoir que, lorsque deux paires de substituants *ortho*-méthyles sont présents, les groupes phényles des stilbénoïdes donneurs sont coaxiaux et on peut les observer spectralement dans les cations radicaux (**2a<sup>+-</sup>-2c<sup>+-</sup>**) par l'apparition de nouvelles bandes de forte intensité dans le proche infrarouge, avec un  $\lambda_{max}$  de 1100–1315 nm, analogues à celles observées antérieurement dans les interactions intermoléculaires (aromatiques) des cations radicaux aromatiques.

Mots clés : hydrocarbure stilbénoïde, cation radical, interaction aryle-aryle.

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## Introduction

The through-space interaction between a pair of vicinal aromatic  $\pi$ -systems is known to decrease the ionization potential in a variety of aromatic hydrocarbons such as 1,1,2,2tetraphenylethane, 1,2-diarylethanes, triptycenes, cyclophanes, benzpinacols, etc. (1-3). In the latter, Penn et al. (4) noted that such cofacial aryl-aryl interactions can explain the increased electron-transfer reactivity in carbon-carbon bond cleavage. Recently, Gano et al. (5) pointed out that similar 1,2-diaryl interactions are also responsible for the observed decrease in the ionization potentials in (Z)-stilbenes as compared to the corresponding (E) isomers. Since these findings suggest that the cation-radical intermediates resulting from 1-electron oxidation of such systems may be unusually stable species, a detailed (UV-vis) spectroscopic analysis of these cationic intermediates must be carried out to further explore the structural requirements of aryl-aryl interactions. As such, the observation of new electronic transitions in multichromophoric assemblies would provide valuable information regarding the spatial (electronic) interactions

amongst the various chromophores. For example, *inter-molecular* interactions of aromatic hydrocarbons (ArH) have been previously observed by the presence of new broad absorption bands in the near-IR region in the electronic absorption spectra of a variety of dimeric aromatic cation radicals (6, 7), and the broad NIR absorption bands have been assigned to charge-resonance transitions within the dimeric cation radicals (ArH)<sub>2</sub><sup>++</sup> arising from the favorable  $\pi$ ,  $\pi$ -orbital overlap between the two coplanar arene moieties arranged in a sandwich-like structure (also compare ref. 8).

In this study, we report the preparation of cation-radical salts of various stilbenoid donors with cofacially juxtaposed aryl groups, and show how analysis of the electronic absorption spectra provides spectroscopic evidence for direct 1,2-diaryl interactions. The two series of stilbenoid donors in Chart 1 are readily synthesized by an efficient palladium-catalyzed synthetic method (9). The spatial arrangements of the neighboring aryl groups in these stilbenoid donors are evaluated by monitoring the UV–vis spectra (and chemical reactivity) and further confirmed by X-ray crystallography. Moreover, the spectral comparison of the cation radical de-

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Chart 1. Stilbenoid donors.



rived from other cofacial  $\pi$ -systems oriented at different dihedral angles (such as *m*-cyclophane and a cofacially oriented phenylene donor) sheds additional light on the angular requirements for such cofacial aryl–aryl interactions.

## **Results and discussion**

#### 1. Synthesis of stilbenoid donors

The various stilbenoid donors in Chart 1 were readily prepared by the palladium-catalyzed coupling of aryl Grignard reagents with a dibromoalkene, e.g.

In a typical example, a freshly prepared solution of phenylmagnesium bromide (2.1 equiv.) was mixed with a solution of 2,3-dibromobicyclo[2.2.2]oct-2-ene in anhydrous tetrahydrofuran containing a catalytic amount of bis(triphenylphosphine)palladium(II) chloride (10) under an argon atmosphere at 25°C. The resulting pale-yellow solution was refluxed for 8 h, and a standard aqueous work-up, followed by recrystallization, afforded 2,3-diphenylbicyclo[2.2.2]oct-2-ene (**1a**) in essentially quantitative yield. The generality of the procedure was demonstrated by coupling various arylmagnesium bromides (with increasing substitution) with dibromobicyclooctene to afford the diarylbicyclooctenes listed in Table 1 in excellent yields.

**Table 1.** Synthesis of various stilbenoid donors by the Pd-catalyzed coupling of arylmagnesium bromides with 1,2-dibromobicyclooctene in tetrahydrofuran.<sup>a</sup>

Stilbenoid hydrocarbon	Time <sup><math>b</math></sup> (h)	% Yield <sup>c</sup>	
1a	8	96	
1b	6	94	
1c	12	92	
1d	12	91	
2a	18	94	
2b	18	94	
2c	24	91	
2d	24	82	

<sup>a</sup>See the experimental section for the general procedure.

<sup>b</sup>The course of the reaction monitored by GC.

#### 2. Conformational analysis of stilbenoid donors

Owing to the rigid backbone structure, the various stilbenoid donors can attain one of the two stable (idealized)

conformations, i.e., face-to-face (cofacial) (11) or edge-toface (perpendicular) (12), as diagrammatically presented in Chart 2. Optimum  $\pi$ - $\pi$  interactions between aryl groups in

Chart 2. Aromatic-aromatic orientations.



various stilbenoid donors are expected to arise from the cofacial arrangement of the aryl groups, and we will determine how such a preferred conformation can be achieved by varying the substituents on the aryl groups as follows.

#### X-ray crystallography

Single crystal structure analysis was performed on **1a** in class A and **2a/2b** in class B in order to ascertain the molecular structures and conformations of the stilbenoid donors. For the sake of simplicity, we identify the structural parameters used for the comparison of all three structures as *d*, the olefinic C=C bond length; *l*, the C–C bond length to the aryl group;  $\theta$ , the twist of the olefinic C=C bond; and  $\phi_1/\phi_2$ , the coplanarity of aryl groups with the C=C bond (as designated in the generic structure in Table 2). (Note that equal values of  $\phi_1$  and  $\phi_2$  indicate that the aryl groups are cofacial.)

Comparison of the various parameters *d*, *l*,  $\theta$ ,  $\phi_1$ , and  $\phi_2$  for **1a**, **2a**, and **2b** in Table 2 shows that the stilbenoid donors (**2a** and **2b**), that contain *ortho*-methyl groups have essentially the same molecular structure that is characterized by the presence of *cofacial* aryl groups. It is clear that steric hindrance of the *ortho*-methyl groups forces both aryl groups to lie parallel to each other and (almost) orthogonal to the ethylenic bond with  $\phi_1 = \phi_2 = 65^\circ$ , and the rotations of the aryl groups (around the C<sub>1</sub>–C<sub>3</sub> and the C<sub>2</sub>–C<sub>5</sub> bonds) are strongly coupled (i.e., mutually dependent), as indicated by the identical values of  $\phi_1$  and  $\phi_2$  in **2a** and **2b**. By contrast, the absence of *ortho*-methyl groups in the parent analog **1a** 

<sup>&</sup>lt;sup>c</sup>Isolated yields.

 Table 2. Comparison of selected structural parameters for various stilbenoid donors.



Parameter	1a	2a	2b
d	1.351(1)	1.328(5)	1.352(1)
$l^a$	1.484(1)	1.51(2)	1.496(1)
$\Theta^b$	$6.6^{\circ}$	4.9°	4.5°
$\phi_1^c$	45.6°	64.8°	59.9°
$\phi_2^{\ d}$	60.1°	65.5	62.1°

<sup>a</sup>Average of two bonds ( $C_1$ – $C_3$  and  $C_2$ – $C_5$ ).

<sup>b</sup>Torsional angle C<sub>3</sub>-C<sub>1</sub>-C<sub>2</sub>-C<sub>5</sub>.

<sup>c</sup>Torsional angle  $C_2$ - $C_1$ - $C_3$ - $C_4$ .

<sup>d</sup>Torsional angle C<sub>1</sub>-C<sub>2</sub>-C<sub>5</sub>-C<sub>6</sub>.

Fig. 1. The superimposition of the molecular structures of diphenyl- (1a, light lines) and dimesityl- (2b, dark lines) bicyclooctenes to show the coplanarity of a single phenyl group with the olefinic bond in 1a.



**Fig. 2**. Space-filling representation of **2a** to show the complete entombment of the olefinic carbons (darkened spheres) by four *ortho*-methyl groups and the bicyclooctene framework.

## $C_3$ or the $C_2$ - $C_5$ bond, as indicated by the different torsion angles $\phi_1$ (46°) and $\phi_2$ (60°).<sup>2</sup> Furthermore, an arbitrary superposition of the molecular structures of **1a** and **2b** (such as that illustrated in Fig. 1<sup>3</sup>) shows that at least one of the phenyl groups in **1a** can readily acquire a coplanar conformation with the olefinic bond.

allows a greater degree of rotational freedom around the C1-

#### Electronic (UV-vis) spectra

Structural analysis (vide supra) reveals that the presence of four *ortho*-methyl groups in various stilbenoid donors in class B forces both aryl groups to lie orthogonal to the olefinic bond, and thus effectively prevents  $\pi$ -conjugation with the olefinic bond. As such, the UV–vis spectral data show that all donors in class B absorb at  $\lambda_{max} < 260$  nm, whereas the class A derivatives show well-defined absorption bands that are relatively red-shifted to  $\lambda_{max} \ge 260-310$  nm (see Experimental). Importantly, the UV–vis absorption spectra of various derivatives in class A are strongly reminiscent of those of the parent stilbenes (14). In contrast, the cofacial stilbenoid donors in class B show absorption spectra that closely resemble those of the *isolated* (non-conjugated) aryl groups.

## Reactivity and steric crowding

The olefinic carbons in class B donors are completely entombed due to the presence of four *ortho*-methyl groups (as well as the bicyclooctene framework), as shown by the spacefilling representation of 2a in Fig. 2. Such steric crowding around the olefinic bonds makes these donors completely inert to hydrogenation and epoxidation reactions. (Note that the



<sup>&</sup>lt;sup>2</sup>Such a restricted rotation around the C–Ar single bond can lead to atropisomers as observed in a variety of biphenyls (ref. 13). For example, spectral (NMR) analysis of naphthyl derivative **1d** showed the presence of two isomers (see Experimental) that could not be separated or interconverted by heating up to 180°C. A (molecular mechanics) minimization of the molecular structure of **2d** with the aid of the QUANTA graphics (Molecular Simulation Inc., 16 New England Executive Park, Burlington, MA 081803) confirmed the presence of two (*syn* and *anti*) atropisomers. An X-ray structural study (in progress) should establish this point.

<sup>&</sup>lt;sup>3</sup>All eight of the carbon atoms of the bicyclooctene moiety in 1a were superimposed on those of 2a for Fig. 1.

1-naphthyl derivative **2d** is similarly unreactive.<sup>4</sup>) In contrast, the class A derivatives (which lack *ortho*-methyl groups) readily undergo hydrogenation and epoxidation reactions owing to a greater rotational freedom of the aryl groups.<sup>4, 5</sup>

## 3. Cation radicals of the stilbenoid donor

## Methods of oxidation

All the stilbenoid donors in Chart 1 undergo reversible electrochemical oxidation in the range  $E_{ox}^0 = 0.98-1.45$  V vs. SCE<sup>6</sup> (see Table 3). The electrochemical reversibility in such an easily accessible potential range allows the ready preparation of the corresponding cation radicals by either chemical or electrochemical oxidation in dichloromethane solution. For example, the chemical oxidation can be readily carried out by electron exchange with stable aromatic cation-radical salts **MA<sup>++</sup>** and **EA<sup>++</sup>**, as selective organic oxidants with reversible reduction potentials that differ by only 190 mV, as listed in Chart 3 (16). Similarly, a mixture of

Chart 3. Cation-radical oxidants.



chloranil and methanesulfonic acid (15) can also serve as an effective oxidant for the preparation of dichloromethane solutions of the cation radicals of the various stilbenoid donors in Chart 1. Moreover, the isolation of crystalline cationradical salts from a number of stilbenoid donors can be effected with triethyloxonium hexachloroantimonate (17) as the 1-electron oxidant (see Experimental). Alternatively, the stable cation-radical solutions from stilbenoid donors in Chart 1 can be obtained by anodic oxidation in anhydrous dichloromethane containing tetrabutylammonium hexafluorophosphate as the supporting electrolyte (see Experimental ).

## Electronic absorption spectra

A solution of stilbenoid derivative 1c when mixed with 1 equiv. of  $MA^{+*}SbCl_6^{-}$  in dichloromethane (under an argon atmosphere at 25°C) immediately turned red, and the UV-vis absorption spectrum showed the characteristic twin absorption bands, at  $\lambda_{max} = 546$  nm (band I) and 880 nm (band II), of dianisylbicycloctene cation radical 1c<sup>+\*</sup>, as shown in Fig. 3a. Quantitative spectral analysis of the magenta solution (log  $\varepsilon_{546} = 4.16$ ) indicated that the electron exchange in eq. [2] was displaced completely to the right, i.e.,

## $[2] \qquad 1c + MA^{+\bullet} \rightarrow 1c^{+\bullet} + MA$

The same exchange procedure was used for the preparation of the UV-vis absorption spectra of the other stilbenoid cation radicals in Fig. 3*a*. It is important to emphasize, however, that the spectra were not dependent on the method of oxidation of the neutral donors, i.e., either electrochemical or chemical oxidation (vide supra). Thus the absorption spectra for the various stilbenoid cation radicals presented in Figs. 3 and 4 were obtained by at least three independent methods of oxidation and found to be the same, as follows.

#### Class A stilbenoid cation radicals

The class A stilbenoid cation radicals showed the characteristic (UV–vis) absorption spectra (in Fig. 3*a*) with twin absorption bands I and II (consisting of similar band shapes and fine structure in the high-energy band). These spectra are strongly reminiscent of the absorption spectrum previously observed for the transient cation radical of the parent (*Z*)-stilbene in frozen matrices (18) (see Fig. 3*b*). Interestingly, a change of the aryl group from phenyl to tolyl to anisyl in class A stilbenoid cation radicals leads to a monotonic red shift in the absorption maxima of both bands I and II as well as a hyperchromic increase in the (relative) intensity of band II. Such an observation is in accord with the increasing stabilization of the cationic charge by a coplanar aryl group containing a *para* substituent (19) in the order:  $H < CH_3 < OCH_3$ 

#### Class B stilbenoid cation radicals

In marked contrast, the various class B stilbenoid cation radicals in Fig. 4a showed an intense new (broad) absorption band (band III) in near-IR region (1100–1315 nm) in addition to the twin absorption bands I and II in the UV–vis region. It is important to reemphasize that the NIR absorption band III was completely absent in all the class A stilbenoid cation radicals, as shown in Fig. 4b.

Such a remarkable difference in the electronic absorption spectra of class A and B stilbenoid cation radicals can be ascribed to the steric effects of the ortho-methyl groups. Thus, in class A derivatives, the absence of ortho-methyl groups allows ready attainment of a conformation (edge-to-face) in which one of the aryl groups is coplanar with the ethylenic bond. However, such a coplanar conformation is strongly discouraged in class B derivatives due to the presence of ortho-methyl groups, and leads to only a face-to-face (cofacial) conformation (for example, see Chart 4). The observation of new electronic absorption bands in the NIR region (band III in Fig. 4a) is thus ascribed to chargeresonance transitions between the rigidly held cofacial aryl groups in 2a-2d cation radicals. Such a spectral assignment is in accord with the observations of Badger and Brocklehurst (6) and Rodgers (7), who showed the presence of in-

<sup>&</sup>lt;sup>4</sup>A palladium-catalyzed hydrogenation of **2d** under high pressure led to a partial reduction of the naphthyl moiety. For the hydrogenation procedures, see R. Rathore et al. (9)

<sup>&</sup>lt;sup>5</sup>A standard epoxidation procedure using *m*-chloroperbenzoic acid was employed, see ref. 15.

 $<sup>{}^{6}(</sup>a)$  Reversible electrochemical oxidation potentials ( $E^{0}_{ox}$  in V vs. SCE) were measured for the various stilbenoid donors (5 mM) by cyclic voltammetry in dichloromethane (containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte). Note that the naphthyl derivative **1d** was irreversibly oxidized even at a scan rate of v = 2 V s<sup>-1</sup>. (*b*) It is noteworthy that  $E^{0}_{ox}$  values of the class B donors are not significantly less positive than those of the class A analogues, despite the presence of additional electron-releasing methyl groups (24). No doubt part of the discrepancy lies in the orthogonal aromatic rings, which completely remove them from ethylene conjugation. We hope to develop other qualitative methods for determining the stabilization energy of the through-space delocalized cation radicals **2a<sup>++</sup>-2c<sup>+</sup>**.

		Cation radical					
Donor		UV-vis band	UV-vis band	IR band			
(D)	$E^0_{ox}{}^b$	$\lambda_{\max}$ (I) <sup>c</sup>	$\lambda_{\max}(II)^c$	$\lambda_{\max}(III)^c$	log ε		
1a	1.47	493, 472(sh)	722	d	d		
1b	1.36	518, 478(sh)	781	d	d		
1c	0.98	547, 506(sh)	880	d	d		
1d	$1.28^{e}$	f	f	f	f		
2a	1.28	426	740	1162	3.87		
2b	1.40	410	681	1100	3.73		
2c	1.21	428	700	1315	3.98		
2d	1.33	534	782	1294	g		
3	0.80	440	460	1200	3.98		
4	1.41	475		1180	g		

Table 3. Cation radicals of various stilbenoid donors in solution.<sup>a</sup>

<sup>*a*</sup>For the oxidation procedures, see Experimental.

 $^{b}\rm V$  vs. SCE at 25°C. In dichloromethane containing 0.2 M n-tetrabutylammonium hexafluorophosphate at 100 mV s^-1.

 $^{c}\lambda_{\max}$  in nm.

<sup>d</sup>No absorption band observed in NIR region.

<sup>*e*</sup>Peak potential, irreversible cyclic voltammogram at v = 1000 mV s<sup>-1</sup>.

<sup>f</sup>Transient cation radical.

<sup>g</sup>Not determined.

**Fig. 3.** (*a*) The UV-vis absorption spectra of various cation radicals from class A stilbenoid donors (as indicated) obtained by oxidation with  $\mathbf{EA}^{++}$  SbCl<sub>6</sub><sup>-</sup> in dichloromethane at 22°C. (*b*) Comparison of the UV-vis absorption spectra of the cation radicals of parent (*Z*)-stilbene (18) and 2,3-diphenylbicyclooctene **1a** (as indicated).



Fig. 4. (a) The pronounced NIR absorption band III in the electronic spectra of the cation radicals from class B stilbenoid donors (as indicated) in the region between  $\lambda_{max} = 1100-1315$  nm in dichloromethane at 22°C. (b) For comparison, the UV-vis absorption spectra of the cation radicals  $1b^{+*}$  and  $1c^{+*}$  showing the absence of the NIR band.



Chart 4. Interplanar dihedral angles.



tense NIR absorption bands in the electronic spectra of a variety of (intermolecular) dimeric aromatic cation radicals. They further suggested that the efficient orbital overlap between the parallel aromatic  $\pi$ -systems (in a sandwich-like structure) is the structural basis for the observed charge-resonance transitions (i.e., NIR absorption bands). Note that a sandwich-like arrangement of the dimeric aromatic cation radicals (of naphthalene and its derivatives) has been verified by isolation of single crystals and their X-ray crystallographic characterization (for a review, see ref. 20).

### Angular requirements for the charge-resonance transitions

Intense charge-resonance absorption bands of the stilbenoid cation radicals **2a**–**2d** are observed despite the fact that the interplanar (dihedral) angle of  $\Psi > 70^{\circ}$  between the two aryl  $\pi$ -systems deviates significantly from that of a parallel arrangement (see Chart 4). To address the question of the angular requirements for observation of chargeresonance transitions in the cation radicals, we extend the donors to a cyclophane (2,4,2',4'-tetramethoxy-*m*-cyclophane, **3** (21)) and a phenylene donor (octamethyl-9,10-dihydro-9,10-ethanoanthracene **4** (22)) in which the cofacial  $\pi$ -systems are oriented at different interplanar  $\Psi$  angles as established by X-ray crystallography (see Chart 4). (Also note that the closest interplanar contacts between two aromatic  $\pi$ -systems in **2a**, **3**, and **4** are 3.08, 2.94, and 2.42 Å, which are much shorter than the sum of van der Waals thickness 2r = 3.4 Å.)

Cyclophane 3 and the phenylene donor 4 undergo reversible electrochemical oxidation in dichloromethane at potentials of  $E_{0x}^{0} = 0.80$  V and 1.41 V vs. SCE, respectively, which are lower by 380 and 230 mV than those of the parent 4,6-dimethyl-1,3-dimethoxybenzene ( $E^0_{ox} = 1.18$  V vs. SCE) (23) and hexamethylbenzene ( $E^0_{ox} = 1.64$  V vs. SCE) (24). Furthermore, the cofacial donors **3** and **4** were both readily oxidized to the corresponding cation radicals by electron exchange with MA+\* and chloranil - methanesulfonic acid mixture (vide supra), and the UV-vis spectral analysis of the yellow-green solutions in both cases showed intense chargeresonance absorption bands at 1200 and 1180 nm, respectively (see Fig. 5). Such an observation of the NIR absorption bands in 2a, 3, and 4, with drastically varied interplanar angles from  $\Psi = 30^{\circ}-117^{\circ}$ , suggests that minimal orbital overlap between interacting  $\pi$ -systems is sufficient for charge-resonance transitions to occur. Thus, a close, but not necessarily complete, cofacial approach of  $\pi$ -systems in various cation radicals (see Chart 4) leads to strong electronic interactions between the two aryl moieties, and results in

**Fig. 5.** The NIR bands in the UV–vis absorption spectra of the cation radicals from cofacial donors **3** and **4** (as indicated) showing the presence of intense charge-resonance bands in the 1200-nm region.



charge-resonance transitions in the UV–vis–NIR absorption spectra similar to those observed for the dimeric cation radicals. Theoretical analysis and quantitative comparison of the (NIR) charge-resonance absorption bands with changes in various structural parameters in a variety of mixed-valence cation-radical salts are currently under investigation.

## **Summary and conclusions**

The efficient synthesis of the stilbenoid donors in Chart 1 allows the steric requirement for the cofacial interaction of aromatic groups to be established. Thus the presence of orthomethyl substituents in the class B donors 2a-2c forces the aromatic rings to lie parallel and orthogonal to the ethylenic bond (Fig. 1). As a result, the electronic (UV-vis) transitions in the cation radicals  $2a^{\text{+}\text{\bullet}}\text{-}2c^{\text{+}\text{\bullet}}$  show strong new absorption bands in the near-IR region (1100 -1315 nm) arising from the charge-resonance interaction between cofacial aromatic rings. However, the energy of such a through-space charge delocalization is not sufficient to overcome the throughbond conjugation inherent to stilbene cation radicals, and the UV-vis spectra of the cation radicals of the class A donors 1a-1d (with no ortho substituents) are singularly bereft of the near-IR absorption. We believe, however, that 1,2-diaryl interactions of the type described for stilbenoids 2a-2c in this study will also pertain to the saturated analogues such as

vicinal diarylalkanes, etc. (1–3), in which restricted (single) bond rotations and through-bond conjugation will be less restrictive.

## Experimental

## Materials

The synthesis of 2,3-dibromobicyclo[2.2.2]oct-2-ene (25), 2, 4, 2', 4'-tetramethoxy-[3.3]-*m*-cyclophane (3) (21), and 1,2,3,4,5,6,7,8-octamethyl-9,10-dihydro-9,10-ethanoanthracene (4) (22) have been described previously. Bis(triphenylphosphine) palladium(II) chloride and triethyloxonium hexachloroantimonate (Aldrich) were stored in a Vacuum Atmosphere HE-493 dry box kept free of oxygen. The cation radicals  $MA^{+*}$  and  $EA^{+*}$  were readily obtained as the stable hexachloroantimonate salts in quantitative yields from the reaction of corresponding neutral hydroquinone ethers **MA** (9,10dimethoxy-1,4:5,8-dimethano-1,2,3,4,5,6,7,8-octahydroanthracene) and **EA** (9,10-dimethoxy-1,4:5,8-dimethano-1,2,3,4,5,6,7,8octahydroanthracene), respectively, with antimony pentachloride (16) or triethyloxonium hexachloroantimonate (17).

## Synthesis of 2,3-diarylbicyclo[2.2.2]oct-2-enes

### General procedure

An approximately 0.4 M solution of pentamethylphenylmagnesium bromide was prepared from bromopentamethylbenzene (5.0 g, 22 mmol) and excess magnesium turnings (2.4 g, 100 mmol) in tetrahydrofuran, under an argon atmosphere by refluxing for 3 h. The Grignard solution thus obtained was transferred via a cannula to a Schlenk flask containing a solution of 2,3-dibromobicyclo[2.2.2]oct-2-ene (25) (2.66 g, 10 mmol) and a catalytic amount of bis(triphenylphosphine)palladium(II) chloride (0.10 g, 0.15 mmol) in anhydrous tetrahydrofuran (20 mL). The resulting yellow mixture was refluxed for 18 h, cooled to room temperature, and quenched with saturated aqueous ammonium chloride (100 mL). The organic layer was separated and the aqueous phase was further extracted with diethyl ether (3  $\times$ 50 mL). The combined organic extracts were washed with water, followed by brine solution, and dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded a pale yellow residue that was filtered through a short pad of silica gel with ether: hexanes (1:1) as the eluent. The resultant product was further purified by recrystallization from ethanol to afford bis(pentamethylphenyl) bicyclooctene 2a as colorless prisms (3.7 g).

The characteristic spectral data for the various diarylbicyclooctenes obtained using the above general procedure are given as follows.

2,3-Diphenylbicyclo[2.2.2]oct-2-ene (1a): Yield 96%, mp 126–127°C (ethanol); UV–vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ : 228, 280 nm; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.68 (sym m, 4H), 1.82 (sym m, 4H), 3.03 (s, 2H), 7.14–7.28 (m, 10H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 26.20, 37.49, 125.85, 127.83, 124.83, 140.23, 141.02; GC–MS m/z, calcd. for C<sub>20</sub>H<sub>20</sub>: 260; found (M<sup>+</sup>): 260. Anal. calcd. for C<sub>20</sub>H<sub>20</sub>: C 92.26, H 7.74; found: C 91.98, H 7.78.

2,3-Bis(4-methylphenyl)bicyclo[2.2.2]oct-2-ene (**1b**): Yield 92%, oil; UV–vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ : 227, 283 nm; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.70 (d, J = 7.5 Hz, 4H), 1.81 (d, J = 7.5 Hz, 4H), 2.40 (s, 6H), 3.04 (br s, 2H), 7.10 (d, J = 8.4 Hz, 4H),

7.14 (d, J = 8.4 Hz, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 21.10, 26.23, 37.52, 128.28, 128.56, 135.26, 138.23, 139.52; GC–MS m/z, calcd. for C<sub>22</sub>H<sub>24</sub>: 288; found (M<sup>+</sup>): 288. Anal. calcd. for C<sub>22</sub>H<sub>24</sub>: C 91.61, H 8.39; found: C 91.45, H 8.35.

2,3-Bis(4-methoxyphenyl)bicyclo[2.2.2]oct-2-ene (1c): Yield 94%, mp 72–73°C (ethanol); UV–vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ : 237, 291 nm; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.62 (br d, 4H), 1.74 (br d, 4H), 2.94 (s, 2H), 3.79 (s, 6H), 6.77 (d, J = 8.7 Hz, 4H), 7.09 (d, J = 8.7 Hz, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 26.23, 37.44, 54.97, 113.23, 129.44, 133.63, 138.60, 157.59; GC–MS *m*/*z*, calcd. for C<sub>22</sub>H<sub>24</sub>O<sub>2</sub>: 320; found (M<sup>+</sup>): 320. Anal. calcd. for C<sub>22</sub>H<sub>24</sub>O<sub>2</sub>: C 82.46, H 7.55; found: C 82.38, H 7.53.

2,3-Bis(2-naphthyl)bicyclo[2.2.2]oct-2-ene (1d): Yield 91%, mp 195–196°C (ethanol); UV–vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ : 270, 315 m; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.73 (d, J = 8.7 Hz, 4H), 1.83 (d, J = 8.7 Hz, 4H), 3.16 (s, 2H), 7.18–7.78 (m, 14 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 26.48, 38.01, 125.44, 125.81, 126.66, 127.20, 127.59, 127.82, 132.07, 133.60, 138.73, 140.85; GC–MS m/z, calcd. for C<sub>28</sub>H<sub>24</sub>: 360; found (M<sup>+</sup>): 360. Anal. calcd. for C<sub>28</sub>H<sub>24</sub>: C 93.29, H 6.71; found: C 93.12, H 6.54.

2,3-Bis(pentamethylphenyl)bicyclo[2.2.2]oct-2-ene (**2a**): Yield 94%, mp 239–240°C (ethanol); UV–vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ : 227, 251 nm; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.77 (br d, J = 7.4 Hz, 4H), 1.91 (br d, J = 7.4 Hz, 4H), 2.14 (s, 12H), 2.18 (s, 6H), 2.19 (s, 12H), 2.63 (br s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 16.63, 16.81, 19.83, 27.28, 37.79, 131.96, 132.08, 132.05, 139.45, 142.71; GC–MS *m*/*z*, calcd. for C<sub>30</sub>H<sub>40</sub>: 400; found (M<sup>+</sup>): 400. Anal. calcd. for C<sub>30</sub>H<sub>40</sub>: C 89.94, H 10.06; found: C 89.77, H 10.01.

2,3-Bis(2,4,6-trimethylphenyl)bicyclo-[2.2.2]oct-2-ene (**2b**): Yield 94%, mp 134–136°C (ethanol); UV–vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ : 225, 258 nm; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.49 (sym m, 8H), 2.16 (s, 12H), 2.20 (s, 6H), 2.64 (s, 2H), 6.74 (s, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 20.71, 21.90, 26.84, 36.65, 128.88, 135.20, 136.23, 138.43, 141.67; GC–MS *m*/*z*, calcd. for C<sub>26</sub>H<sub>32</sub>: 344; found (M<sup>+</sup>): 344. Anal. calcd. for C<sub>26</sub>H<sub>32</sub>: C 90.64, H 9.36; found: C 90.49, H 9.19.

2,3-Bis(2,6-dimethyl-4-methoxyphenyl)bicyclo[2.2.2]oct-2-ene (2c): Yield 91%, mp 129–130°C (ethanol); UV–vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ : 221, 260 nm; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.79 (br s, 8H), 2.23 (s, 12H), 2.67 (s, 2H), 3.76 (s, 6H), 6.54 (s, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 22.41, 27.03, 36.91, 54.98, 113.45, 134.20, 137.98, 141.64, 157.30; GC–MS *m*/*z*, calcd. for C<sub>26</sub>H<sub>32</sub>O<sub>2</sub>: 376; found (M<sup>+</sup>): 376. Anal. calcd. for C<sub>26</sub>H<sub>32</sub>O<sub>2</sub>: C 82.94, H 8.57; found: C 82.69, H 8.73.

2,3-Bis(1-naphthyl)bicyclo[2.2.2]oct-2-ene (2d), a mixture of atropoisomers:<sup>2</sup> Yield 82%, mp 186–188°C (ethanol); UV–vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$ : 231, 296 nm; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.75–2.00 (m) and 2.13 (d, J = 7.2 Hz, 8H), 2.96 and 3.03 (two singlets, 2H), 7.00–8.12 (m, 14H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 26.12, 26.64, 27.55, 28.28, 37.49, 38.37, 125.21, 1225.45, 125.53, 125.68, 126.35, 126.46, 126.60, 126.68, 126.78, 128.83, 128.29, 12.56, 132.14, 133.78, 133.84, 140.04, 140.38, 142.23, 143.88; GC–MS *m*/*z*, calcd. for C<sub>28</sub>H<sub>24</sub>: 360; found (M<sup>+</sup>): 360. Anal. calcd. for C<sub>28</sub>H<sub>24</sub>: C 93.29, H 6.71; found: C 93.04, H 6.64.

Dichloromethane (Mallinckrodt analytical reagent) was repeatedly stirred with fresh aliquots of concentrated sulfuric acid (~20% by volume) until the acid layer remained colorless. After separation, it was washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride, and dried over anhydrous calcium chloride. The dichloromethane was distilled twice from  $P_2O_5$  under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. The hexane and toluene were distilled from  $P_2O_5$  under an argon atmosphere and then refluxed over calcium hydride (~12 h). After distillation from CaH<sub>2</sub>, the solvents were stored in the Schlenk flasks under an argon atmosphere.

#### Instrumentation

The UV–vis absorption spectra were recorded on HP 8453 diode array and Varian CARY 5 (UV–vis–NIR) spectrometers. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a General Electric QE-300 FT NMR spectrometer. Electrochemical apparatus and the procedures for the determination of oxidation potentials and for the preparation of cation radicals have been described elsewhere (9).

## Oxidation of various stilbenoid donors

## General procedure

A stock solution of  $EA^{+*}$  ( $\lambda_{max}=486$  nm, log  $\epsilon_{486}=3.66$   $M^{-1}~cm^{-1}$ ) was obtained by dissolving a known quantity of  $\mathbf{EA^{+}SbCl_6^{-}}$  (4.25 mg, 6.92 × 10<sup>-5</sup> mmol) in anhydrous dichloromethane (50 mL) at 22°C and under an argon atmosphere. A 5 mL aliquot of the red-orange solution was transferred to a 1 cm quartz cuvette equipped with a Schlenk adapter (under an argon atmosphere). A solution of the stilbenoid donor 2c (1 equiv.) was added at 25°C. The reaction mixture immediately turned bright green and the UV-vis spectral analysis confirmed the formation of  $2c^{+\bullet}$  ( $\lambda_{max} = 428$ , 700, and 1315 nm, log  $\varepsilon_{1315} = 3.98 \text{ M}^{-1} \text{ cm}^{-1}$ ). In a similar manner, various stilbenoid donors in Chart 1 were quantitatively oxidized to corresponding cation radicals, and the UV-vis absorption maxima are compiled in Table 3. Various donors with  $E_{\text{ox}}^0 < 1.2$  V vs. SCE were readily oxidized with  $\mathbf{MA^{+}}$ ( $\lambda_{\text{max}} = 518$  nm, log  $\varepsilon_{518} = 3.86$  M<sup>-1</sup> cm<sup>-1</sup>, whereas donors with  $E_{\text{ox}}^0 > 1.2$  V were oxidized with  $\mathbf{EA^{+}}$  ( $\lambda_{\text{max}} = 518$  nm,  $\log \epsilon_{486} = 3.66 \text{ M}^{-1} \text{ cm}^{-1}$ ). Oxidation procedures with chloranil - methanesulfonic acid (method B) (15) and triethyloxonium hexachloroantimonate (method C) (17) have been described in detail.

## Preparative isolation of stilbenoid cation radical salts using $Et_3O^+$ SbCl<sub>6</sub><sup>-</sup>

A 200 mL flask equipped with a Schlenk adapter was charged with triethyloxonium hexachloroantimonate (657 mg, 1.5 mmol), and a solution of **1c** (320 mg, 1 mmol) in anhydrous dichloromethane (25 mL) was added under an argon atmosphere at  $-20^{\circ}$ C. The heterogeneous mixture immediately took on magenta coloration, which intensified with time. The dark-red mixture was stirred for 1 h to yield a magenta-red solution of **1c**<sup>+•</sup> ( $\lambda_{max}$  (nm) = 546, 880; see

Fig. 3*a*). The dark magenta solution was cooled to  $-50^{\circ}$ C in an Dry Ice – acetone bath, and anhydrous toluene (100 mL) was added to precipitate the dissolved salt. The dark-red precipitate was filtered under an argon atmosphere, washed with hexane (3 × 25 mL), and dried in vacuo. The cation radical  $1c^{+*}$  SbCl<sub>6</sub><sup>-</sup> (vide infra) was obtained in essentially quantitative yield (550 mg, 0.84 mmol).

The purity of the isolated cation radical  $1c^{+*}$  SbCl<sub>6</sub><sup>-</sup> was determined by iodometric titration as follows. A solution of  $1c^{+*}$  SbCl<sub>6</sub><sup>-</sup> (65.5 mg, 0.01 M) in dichloromethane was added to a dichloromethane solution containing excess tetra-*n*-butylammonium iodide (1 mmol, 0.1 M) at 22°C, under an argon atmosphere, to afford a dark-brown solution. The mixture was stirred for 5 min and was titrated (with rapid stirring) by slow addition of a standard aqueous sodium thiosulfate solution (0.005 M) in the presence of a starch solution as internal indicator. Based on the amount of thiosulfate solution consumed (57.4 mL), purity of the cation radical was determined to be >97%. With the same procedure, the crystalline cation radical salts of **2a** and **2c** were also isolated in 76 and 81% yields, respectively.

## X-ray crystallography

The intensity data for all the compounds were collected with the aid of a Siemens SMART diffractometer equipped with a CCD detector using Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å), at  $-150^{\circ}$ C unless otherwise specified. The structures were solved by direct methods (26) and refined by full-matrix least-squares procedure with IBM Pentium and SGI Indigo computers. The details of the X-ray structure of the various compounds have been deposited.<sup>7</sup>

### 2,3-Diphenylbicyclo[2.2.2]oct-2-ene (1a) ( $C_{20}H_{20}$ )

An X-ray quality crystal ( $0.20 \times 0.20 \times 0.20$  mm) of diphenylbicyclooctene was obtained from an ethanol–dichloromethane mixture at  $-30^{\circ}$ C. MW = 260.36, orthorhombic, space group  $P2_12_12_1$ , a = 6.0645(1), b = 12.1491(3), and c = 19.4396(5)Å,  $D_c = 1.207$  Mg m<sup>-3</sup>, V = 1432.28(6) Å<sup>3</sup>, Z = 4. The total number of reflections measured were 6492, of which 6492 reflections were symmetrically non-equivalent. Final residuals were R1 = 0.0477 and wR2 = 0.1017 for 6492 reflections with  $I > 2\sigma$  (I).

# 2,3-Bis(pentamethylphenyl)bicyclo[2.2.2]oct-2-ene (2a) $(C_{30}H_{40})$

An X-ray quality crystal  $(0.3 \times 0.2 \times 0.1 \text{ mm})$  of **2a** was obtained from an ethanol–dichloromethane mixture at  $-30^{\circ}$ C. MW = 400.62, monoclinic, space group  $P2_1/n$ , a = 8.6608(7), b = 13.223(1), and c = 20.401(2) Å,  $\beta = 91.519(2)^{\circ}$ ,  $D_c = 1.139$  Mg m<sup>-3</sup>, V = 2335.6(3) Å<sup>3</sup>, Z = 4. The total number of reflections measured were 8416, of which 3237 reflections were symmetrically non-equivalent. Final residuals were R1 = 0.0730 and wR2 = 0.1259 for 3073 reflections with  $I > 2\sigma(I)$ .

<sup>&</sup>lt;sup>7</sup>Supplementary material, including tables of crystal data and structure refinement, atomic coordinates, isotropic and anisotropic displacement parameters, and bond lengths and angles for 2,3-diphenylbicyclo[2.2.2]oct-2-ene (**1a**), bis(pentamethylphenyl)bicyclooct-2-ene (**2a**), bis(2,4,6-trimethyl-phenyl)bicyclooct-2-ene (**2b**), and 2,4,2',4'-tetramethoxy-*m*-cyclophane (**3**)-chloranil molecular complex may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Canada, K1A 0S2. With the exception of the anisotropic displacement parameters, this material has also been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from: The Director, Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

2,3-Bis(2,4,6-trimethylphenyl)bicyclo-[2.2.2]oct-2-ene (**2b**)  $(C_{26}H_{32})$ 

An X-ray quality crystal ( $0.5 \times 0.4 \times 0.2$  mm) of **2b** was obtained from an ethanol–dichloromethane mixture at  $-30^{\circ}$ C. MW = 344.52, orthorhombic, space group *Pbcn*, *a* = 21.6486(1), *b* = 8.7822(1), and *c* = 21.7995(2) Å, *D<sub>c</sub>* = 1.104 Mg m<sup>-3</sup>, *V* = 4144.57(6) Å<sup>3</sup>, *Z* = 8. The total number of reflections measured were 50 440, of which 9646 reflections were symmetrically non-equivalent. Final residuals were *R*1 = 0.0584 and *wR*2 = 0.1342 for 9638 reflections with *I* > 2 $\sigma$  (*I*).

2,4,2',4'-Tetramethoxy-[3.3]-m-cyclophane (3)–chloranil molecular complex ( $C_{22}H_{28}O_4$ · $C_6Cl_4O_2$ ).

X-ray quality crystals  $(0.35 \times 0.30 \times 0.20 \text{ mm})$  of the charge-transfer complex of **3**-chloranil were obtained by slow evaporation of a equimolar solution of **3** and chloranil in dichloromethane at 25°C. MW = 602.30, orthorhombic, space group *Pnma*, a = 13.464(3), b = 20.144(4), and c = 10.033(2) Å,  $D_c = 1.470$  Mg m<sup>-3</sup>, V = 2721.1(9) Å<sup>3</sup>, Z = 4. The total number of reflections measured were 6618, of which 2161 reflections were symmetrically non-equivalent. Final residuals were R1 = 0.0388 and wR2 = 0.0948 for 2153 reflections with  $I > 2\sigma(I)$ . (Note that the molecular structure of the cyclophane moiety in the **3**-chloranil complex is quite similar to that previously observed for the uncomplexed cyclophane (21).)

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