

# Resonance Raman studies of phenylcyclopropane radical cations

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**Resonance Raman spectra of the radical cations of phenylcyclopropane and *trans*-1-phenyl-2-methylcyclopropane are reported. A near-UV pump pulse excites a photosensitizer which oxidizes the species of interest, and a visible probe pulse delayed by 35 ns obtains the spectrum of the radical ion. The transient Raman spectra of the phenylcyclopropane radical cations show nine or ten enhanced modes for which assignments are suggested based on density functional theory (DFT) results, previously published calculations on the resonant excited state and comparison between the unsubstituted and methyl-substituted compounds. The transient spectra are consistent with the large effect of methyl substitution on the geometry of the radical cation predicted by DFT. The resonance Raman spectrum of the electron donor–acceptor complex between phenylcyclopropane and tetracyanoethylene is also obtained on resonance with the visible charge-transfer absorption band, but the spectra are very weak and only a few resonance enhanced lines are observed. These results are compared with previously published data on the *p*-methoxybenzyltrimethylsilane charge-transfer complex and radical cation. Copyright © 2000 John Wiley & Sons, Ltd.**

## INTRODUCTION

Pump–probe spontaneous resonance Raman spectroscopy has long been recognized as one of the most valuable probes of molecular structure of excited electronic states or other photogenerated transient species having lifetimes in the range from picoseconds to milliseconds.<sup>1</sup> If the transient species has an electronic absorption in the region where the precursor does not, the selectivity available through resonance enhancement often allows a spectrum of the transient to be obtained with little interference from other species even if its concentration is fairly low. Organic radical ions, particularly cations, have been popular targets of such studies because they tend to have strong optical absorptions at much longer wavelengths than the corresponding neutral parents.<sup>2–10</sup> Essentially all of the previous vibrational spectroscopic studies of organic radical ions have been on relatively unreactive ions. Our interests lie in the bond breaking and making reactions of reactive radical cations.<sup>11–17</sup> These reactions have traditionally been examined through product studies and

kinetic and thermodynamic measurements, but these techniques do not yield structural information, such as the changes in the lengths of the bonds that are eventually broken in the radical ions, that is essential for a detailed description of the reaction mechanism. For this reason, we initiated a study of the Raman spectroscopy of a series of reactive radical cations to explore the extent to which this technique could provide useful structural information on these intermediates. The anticipated difficulty is that while it is often possible to obtain high-quality vibrational spectra of moderately complex organic radical ions through transient Raman spectroscopy, the vibrational assignments needed to draw structural conclusions are far more problematic. This is particularly true in the very systems that are of greatest interest, i.e. reactive systems in which the structural changes caused by oxidation or reduction are presumably large, and the vibrational spectrum of the ion is consequently very different from that of the corresponding neutral.

The traditional approaches to assigning the vibrational spectra of complex molecules include utilizing both Raman and infrared spectra (often difficult or impossible with short-lived intermediates present at low concentrations), comparison with spectra of model compounds and isotopic substitution. Recently, computational methods have advanced to the point where calculated vibrational spectra can be useful in making assignments even for fairly large molecules. Methods based on density functional theory (DFT) are proving to yield particularly accurate and reliable vibrational wavenumbers.<sup>18–23</sup> DFT in its usual formulation can be applied only to the ground electronic state of a particular spin multiplicity, but this is not a problem for computations on radical ions, which are

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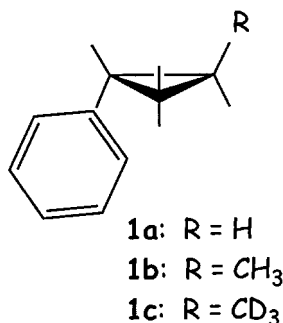
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not electronically excited states although they are transient species.

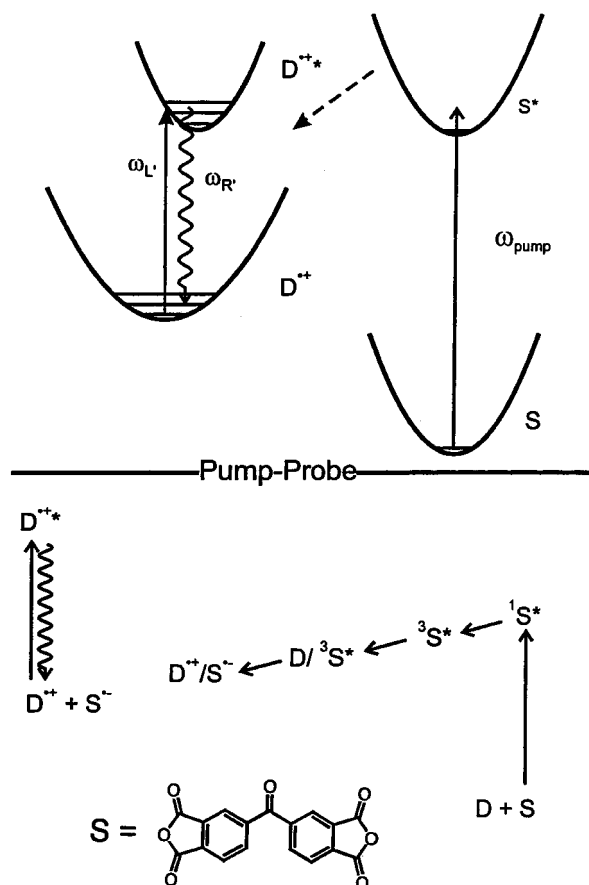
We recently reported a study of the radical cations of *p*-methoxybenzyltrimethylsilane by utilizing a combination of steady-state and transient resonance Raman spectroscopy together with density functional calculations.<sup>7</sup> The silanes are of interest because they undergo rapid C—Si bond cleavage upon oxidation to the radical cation via a nucleophilic  $S_N2$  mechanism.<sup>16</sup> Resonance Raman spectra were obtained for both the neutral charge-transfer complex of the silane with tetracyanoethylene in steady-state continuous-wave (cw) experiments and the silane radical cation via two-color pump-probe transient measurements. The ground-state charge-transfer resonant spectra exhibited intensity predominantly in phenyl-localized modes, suggesting that vertical excitation to the contact ion-pair state involves little participation of the bond that becomes highly reactive in the separated radical cation. In contrast, the transient spectrum of the relaxed silane radical cation showed that the modes having significant contributions from the C—Si stretching coordinate are considerably lower in wavenumber in the radical cation than in the neutral, indicating weakening of this bond upon oxidation. The experimental wavenumbers of both neutral and cation were reproduced fairly well by DFT calculations at the B3LYP/6-31G(d,p) level. This paper extends that work to another class of reactive organic radical cations, the phenylcyclopropanes ( $1^{+\bullet}$ ), which exhibit efficient nucleophilic ring-opening upon oxidation.<sup>12,24-26</sup>

## EXPERIMENTAL AND COMPUTATIONAL METHODS

The sensitizer, 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), was obtained from Aldrich, recrystallized several times from 10:1 benzene-acetic anhydride and vacuum dried overnight. Phenylcyclopropane (**1a**) was obtained from Aldrich; *trans*-1-methyl-2-phenylcyclopropane (**1b**) and its trideuteriomethyl derivative (**1c**) were synthesized as described previously.<sup>26</sup> Tetracyanoethylene (TCNE) was obtained from Aldrich and sublimed under vacuum three times before use.



Resonance Raman spectra of the radical cations were acquired using the second and third harmonics of a Q-switched Nd:YAG laser (Spectra-Physics GCR 150-30). The pump pulse (355 nm, 0.3 mJ per pulse) was used to photoexcite BTDA, which oxidizes the phenylcyclopropane to produce its radical cation (Fig. 1). The probe pulse (532 nm, 0.13 mJ per pulse), generated by the same



**Figure 1.** Scheme used to generate and measure the resonance Raman spectra of the phenylcyclopropane radical cations.

laser, was delayed by 35 ns. The beams were recombined using a dichroic beamsplitter and focused into the sample, contained in a stirred 1 cm fused-silica cuvette. The Raman scattering was collected in backscattering geometry, focused with a fused-silica lens and passed through a quartz polarization scrambler before being dispersed by a Spex 500M 0.5 m single spectrograph. A holographic supernotch filter (Kaiser Optical Systems) was used to exclude stray laser light. The Raman scattered light was detected with a Princeton Applied Research 1461 intensified photodiode array operating at approximately  $-30^\circ\text{C}$ . A PAR 1302 fast pulser was used to gate the detector (20 ns window) with the probe pulse in order to discriminate against fluorescence induced by the pump pulse. In all experiments, 20 mM solutions of both BTDA and the phenylcyclopropane in acetonitrile were used. The optical densities of the samples at 355 nm were about 2.5 per cm.

Resonance Raman spectra of the charge-transfer complex of **1a** with TCNE in dichloromethane were obtained using the general setup described previously.<sup>7</sup> The sample was contained in a rotating cell, excitation was provided by ca 10 mW of cw power from 488 nm radiation from a Lexel argon ion laser, and the detection system was a Spex 1877 triple spectrograph with a Spex liquid nitrogen-cooled CCD. The solutions were prepared to be 60 mM in both donor and acceptor. Spectra of 60 mM donor alone and 60 mM acceptor alone in dichloromethane were also measured for comparison. The spectra were calibrated in wavenumber using known solvent lines as a reference. Because of the weakness of the charge-transfer resonance Raman spectra compared with those we have

studied previously,<sup>27</sup> no attempt was made to determine the absolute Raman cross-sections accurately or to carry out any quantitative analysis of the spectra. Non-resonant Raman spectra of the uncomplexed neutral ground-state species were obtained with the same setup except that the pure liquids were contained in stationary glass capillaries and the excitation source was 514.5 nm radiation from an argon ion laser.

Transient absorption spectra of the radical cations were obtained by exciting the BTDA–phenylcyclopropane solutions with the third harmonic (355 nm) of a mode-locked Q-switched Nd:YAG laser (Continuum, 30 ps pulse width, 10 Hz repetition rate). The absorption spectra were obtained using a white-light continuum pulse generated from self-phase modulation of the fundamental output (1064 nm) of the same laser. The probe pulse was delayed by 32 ns using a fiber optic. Spectra were collected with a thermoelectrically cooled dual diode array (Princeton Instruments).

DFT calculations were performed using Gaussian 94.<sup>28</sup> Geometry optimizations and wavenumber calculations were performed using the Gaussian 94 implementation of the B3LYP hybrid density functional<sup>29</sup> with the 6–311G(d,p) basis set. The normal modes were visualized using XMol 1.3.1.<sup>30</sup>

## RESULTS

The non-resonant Raman spectra of **1a**, **1b** and **1c**, which have not to our knowledge been published before, are shown in Figs 2–4. Table 1 summarizes the observed Raman wavenumbers of the neutral phenylcyclopropanes.

The transient absorption spectrum of **1a**<sup>+</sup> is presented in Fig. 5. The radical cation has a reasonably strong absorption that is well in resonance with the 532 nm probe wavelength employed in the Raman experiments.

Figures 6 and 7 show the transient resonance Raman spectra of **1a**<sup>+</sup> and **1b**<sup>+</sup>. The transient spectra of the phenylcyclopropanes exhibit fewer Raman lines and the strongest lines have qualitatively lower relative intensities than in the corresponding *p*-methoxybenzyltrialkylsilane spectra measured under the same experimental conditions.<sup>7</sup> While differences in pump–probe beam overlap from one experiment to the next could contribute to the differences in apparent transient Raman intensity, the phenylcyclopropane radical cations do appear to be weaker Raman scatterers than the silanes, at least with 532 nm excitation, despite the fact that the transient absorption spectra exhibit similar optical density changes.

Table 2 summarizes the observed vibrational wavenumbers of the radical cations. Nine or ten lines are observed in the region from 400 to 1600 cm<sup>-1</sup>. The two strongest vibrations, at 1596 and 1483 cm<sup>-1</sup> in **1a**<sup>+</sup> (1582 and 1488 cm<sup>-1</sup> in the methyl-substituted compound), are assigned as largely the phenyl-localized modes 8a and 19a, although the calculations indicate the 1483/1488 cm<sup>-1</sup> line also has some phenyl–cyclopropyl stretching character (and cyclopropyl–CH<sub>3</sub> stretching in **1b**<sup>+</sup>). Other Raman lines of the radical ions could be masked by the strong solvent scattering in the regions around 340–410, 900–940, and 1340–1470 cm<sup>-1</sup>. The vibrations involving cyclopropyl C–C stretching are less easily identified in **1**<sup>+</sup> than are those associated with C–Si stretching in our previous study of the silanes,<sup>7</sup> both because fewer resonance-enhanced vibrations are observed and because of the absence of <sup>13</sup>C data for the phenylcyclopropanes. Significant wavenumber or intensity changes between the unsubstituted and methyl-substituted radical cations are seen in the lines of **1a**<sup>+</sup> at 543, 970, 1102, 1188 and 1596 cm<sup>-1</sup> and of **1b**<sup>+</sup> at 449, 820, 971, 1090, 1180 and 1582 cm<sup>-1</sup>.

The DFT calculations provide additional assistance in assigning the vibrations. The assignments given in Tables 1 and 2 are based on comparison of experimental

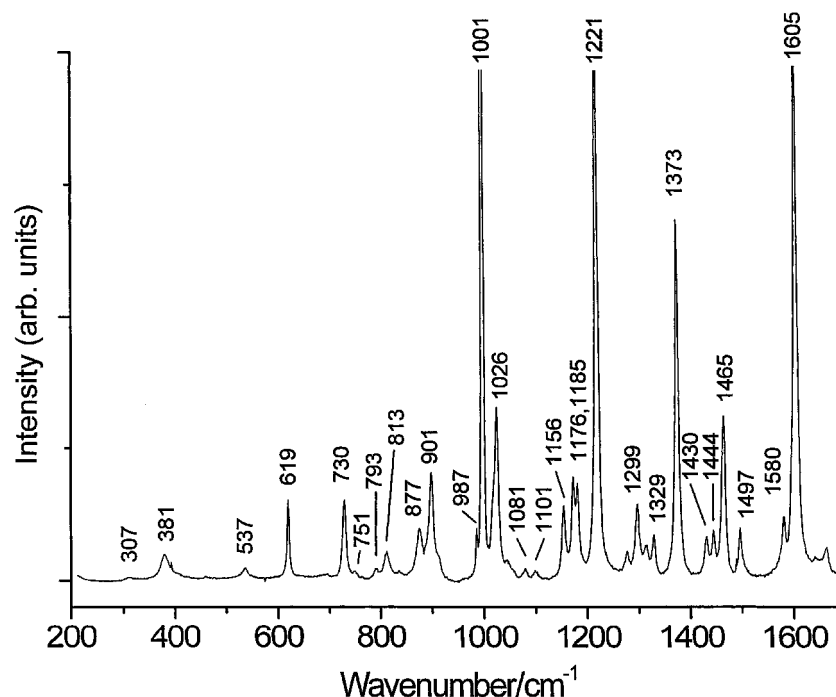


Figure 2. Non-resonant Raman spectrum (514.5 nm excitation) of neat phenylcyclopropane (**1a**).

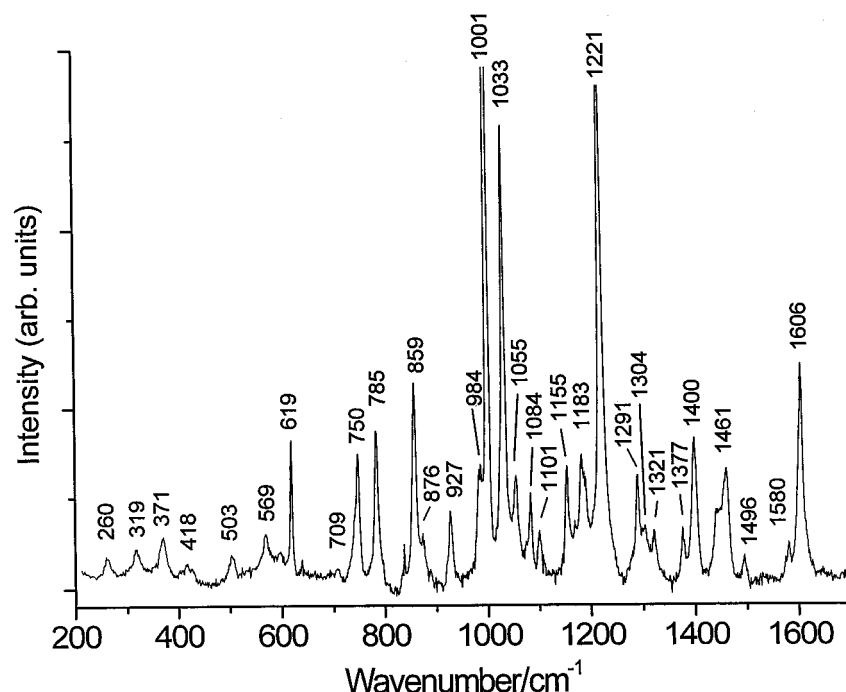


Figure 3. Non-resonant Raman spectrum (514.5 nm excitation) of neat *trans*-1-phenyl-2-methylcyclopropane (**1b**).

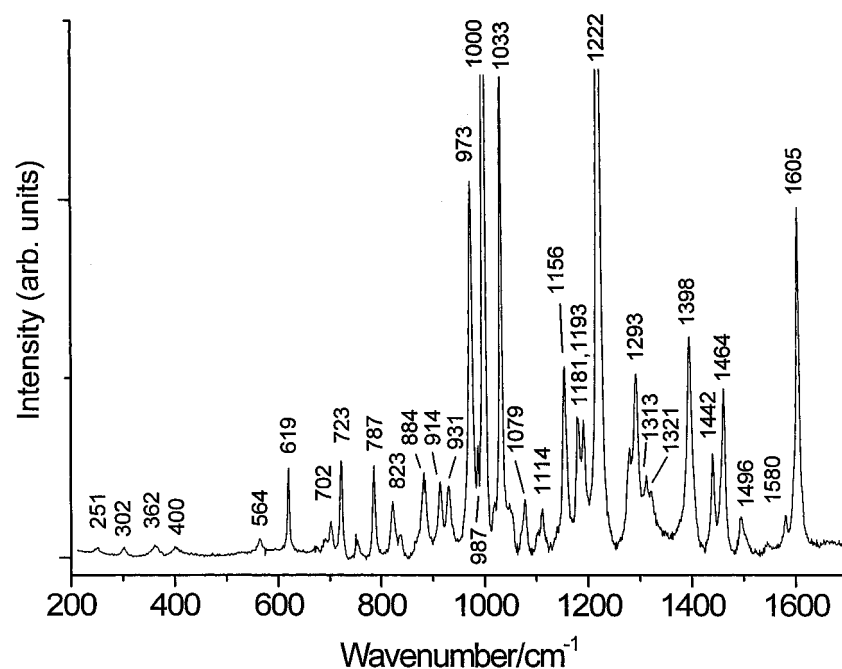


Figure 4. Non-resonant Raman spectrum (514.5 nm excitation) of neat *trans*-1-phenyl-2-methyl- $d_3$ -cyclopropane (**1c**).

and calculated wavenumbers, qualitative non-resonant Raman intensities for the neutrals and comparison with published assignments for other mono- and disubstituted benzenes<sup>31</sup> and substituted cyclopropanes.<sup>32,33</sup> The assignments, particularly for the radical cations, must be considered very tentative. Most of the observed lines could plausibly be assigned to any one of several calculated modes, and comparison of the methyl-substituted and unsubstituted species is complicated by the large changes in wavenumber and normal mode character of many of the vibrations as well as the symmetry breaking caused by methyl substitution. The DFT calculations on **1a** and **1a**<sup>+</sup> predict a dramatic shortening of the cyclopropyl C<sub>8</sub>—C<sub>9</sub>

bond (atom numbering as in Figs 8–11) from 1.51 Å in the neutral to 1.45 Å in the radical cation and of the C<sub>1</sub>—C<sub>7</sub> bond from 1.50 to 1.43 Å, while the C<sub>7</sub>—C<sub>8</sub> and C<sub>7</sub>—C<sub>9</sub> cyclopropyl bonds are calculated to lengthen from 1.51 to 1.59 Å upon oxidation. Methyl substitution is calculated to have little effect on the cyclopropyl ring bond lengths in the neutral molecule but a very large effect on the radical cation, with the C<sub>7</sub>—C<sub>9</sub> bond lengthening only slightly to 1.52 Å upon oxidation whereas the C<sub>7</sub>—C<sub>8</sub> bond length increases to 1.74 Å. The calculated equilibrium geometries of **1a**, **1a**<sup>+</sup>, **1b** and **1b**<sup>+</sup> are shown in Figs 8–11. These predictions are consistent with the large differences between the transient Raman spectra of **1a**<sup>+</sup> and **1b**<sup>+</sup>.

**Table 1. Experimental and calculated wavenumbers ( $\tilde{\nu}$ ) of vibrations of 1a, 1b and 1c**

1a $\tilde{\nu}/\text{cm}^{-1}$		1b $\tilde{\nu}/\text{cm}^{-1}$		1c $\tilde{\nu}/\text{cm}^{-1}$		Possible assignment <sup>c</sup>
Expt. <sup>a</sup>	Calc. <sup>b</sup>	Expt. <sup>a</sup>	Calc. <sup>b</sup>	Expt. <sup>a</sup>	Calc. <sup>b</sup>	
307vw	309	260vw	278	251vw	258	cp-CH <sub>3</sub> bend
		319vw	297	302vw	294	Ph-cp relative bend
		371w	359	362vw	336	Ph 10b, cp-Ph bend
381w	415					cp-CH <sub>3</sub> bend, cp-Ph bend
						Ph 16a
537vw	567	418vw	451	400vw	443	cp and cp-Ph CCCbend
		503vw	494			Ph 16b
619m	635	569w	586	564w	583	Ph 6a [cp def]
		619m	635	619m	635	Ph 6b
		709vw	715			Ph 4
730m	736					Ph 1
		750m	742	723m	726	Ph-cp str, Ph 6a [cp def]
751vw	768					Ph 11
		785m	805	702w	720	cp def
793vw	811					cp CH <sub>2</sub> rock
813w	826					cp CH and CH <sub>2</sub> def
877m	858		857		857	Ph 10a
901m	914	859m	874	787m	803	cp C <sub>8</sub> -C <sub>9</sub> stretch
		876w	903	884m	913	cp C <sub>7</sub> -C <sub>8</sub> stretch
987w	1001		931	914m	930	Ph 17b
			936	823w	837	cp CH wagging
		984w	1000	987w	1002	Ph 5
		~990w	1012	931m	967	Ph 1, cp C <sub>7</sub> -C <sub>9</sub> str, cp-CH <sub>3</sub> str
1001vs	1018	1001vs	1018	1000vs	1018	Ph 12
1026m	1048	1033s	1050	1033s	1044	Ph 18a
		1055m	1067			cp CH <sub>2</sub> rock
1081vw	1083	1084m	1090	973s	997	cp asym def [cp CH <sub>3</sub> r-str]
1101vw	1103	1101w	1109	1102vw	1109	Ph 18b
				1114w	1136	cp CH wag
1156m	1181	1155m	1181	1156m	1181	Ph 9b
1176m	1197	~1172m	1195			cp CH, CH <sub>2</sub> [CH <sub>3</sub> ] def
1185m	1201	1183m	1200	1181w	1200	Ph 9a
		~1190w	1212	1193w	1213	cp-Ph str, cp ring breath
1221s	1250	1221s	1249	1222s	1249	cp breath, Ph-cp str
1299m	1319	1291m	1319	1293m	1319	Ph 14
		1304w	1344	1313w	1339	cp CH rock
1329w	1352	1321w	1351	1321vw	1351	Ph 3
1373s	1393					Ph 13
		1377w	1414			cp CH <sub>3</sub> umbrella
		1400m	1434	1398m	1428	cp-CH <sub>3</sub> , cp-Ph str, cp breath
1430w	1469					cp CH <sub>2</sub> def
1444w	1477	~1445m	1476	1442m	1476	Ph 19b
1465m	1508	~1455m	1495	1464m	1497	cp breath, cp CH <sub>2</sub> def
		1461m	1507	1079w	1082	cp CH <sub>3</sub> def, cp breath
1497w	1531	1496w	1530	1496w	1530	Ph 19a
1580w	1622	1580w	1621	1580w	1621	Ph 8b
1605s	1647	1606s	1646	1605s	1646	Ph 8a

<sup>a</sup> Non-resonant Raman wavenumber of the neat liquid.

<sup>b</sup> Unscaled wavenumber from DFT calculation [B3LYP functional, 6-311G(d,p) basis].

<sup>c</sup> Qualitative description of calculated normal mode. Phenyl-localized modes are denoted by the convention of Varsanyi.<sup>31</sup> Atoms are numbered as in Figs 8 and 10. Brackets indicate internal coordinates that contribute substantially only in 1b and 1c.

The dramatic effects of alkyl substitution on the structures of phenylcyclopropyl radical cations are discussed in more detail in Ref. 26.

Figure 12 displays the resonance Raman spectrum of the 1a:TCNE charge-transfer complex. The visible charge-transfer absorption of this complex is clearly composed of two bands of fairly comparable intensity,<sup>34</sup> and the 488 nm Raman excitation wavelength employed is near the maximum of the redder of these two bands. Even though both donor and acceptor concentrations were near

their limits of solubility, only weak enhancement of a few lines is observed in the complex compared with uncomplexed donor and acceptor. This can be explained by the combination of a small equilibrium constant for complex formation and a modest molar absorptivity for the complex; other things being equal, the resonance Raman intensity of a given species is proportional to its concentration and to the square of its molar absorptivity (fourth power of the electronic transition moment). The product  $\varepsilon^2 K_{\text{eq}}$  is only about  $2 \times 10^6 \text{ M}^{-3} \text{ cm}^{-2}$  for the 1:TCNE

complex in dichloromethane,<sup>34</sup> more than three orders of magnitude smaller than for hexamethylbenzene:TCNE in CCl<sub>4</sub><sup>35</sup> and more than a factor of two smaller than for *p*-methoxybenzyltrimethylsilane:TCNE in CH<sub>2</sub>Cl<sub>2</sub>.<sup>7</sup> The only phenylcyclopropane vibrations clearly enhanced by charge-transfer resonant excitation are the lines at 1026, 1185 and 1605 cm<sup>-1</sup>, which are all assigned as phenyl-localized vibrations. There may be slight enhancement of the 1465 cm<sup>-1</sup> line assigned partly to cyclopropyl ring breathing, but it is weak and difficult to confirm.

## DISCUSSION

This paper builds on our previous work on the silanes<sup>7</sup> in which we outlined two very different ways to use

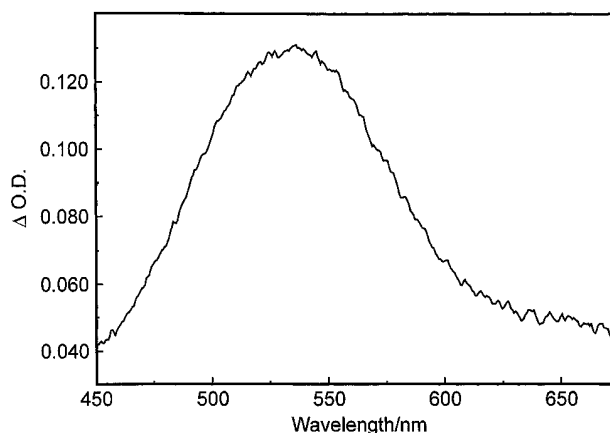


Figure 5. Transient absorption spectrum of the radical cation of phenylcyclopropane (**1a**) in acetonitrile.

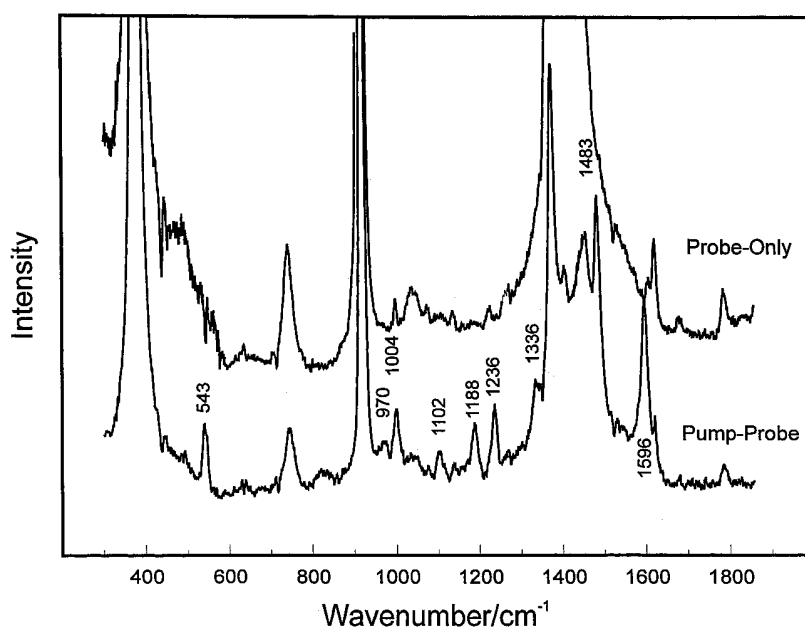


Figure 6. Probe-only and pump-probe Raman spectra of a solution of 20 mM BTDA and 20 mM phenylcyclopropane (**1a**) in acetonitrile. Pump and probe wavelengths are 355 and 532 nm, respectively. Labeled peaks are assigned to **1a**<sup>•+</sup>.

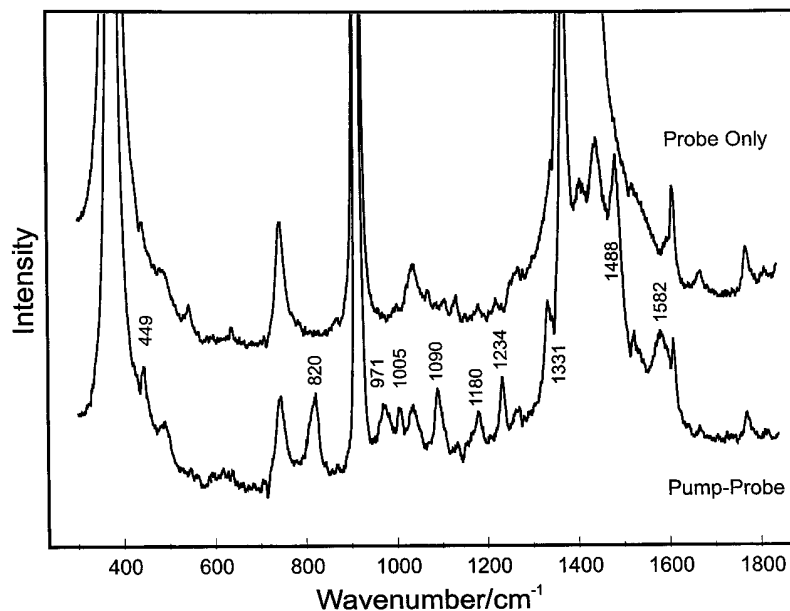


Figure 7. Same as Fig. 6 for *trans*-1-phenyl-2-methylcyclopropane (**1b**) in acetonitrile.

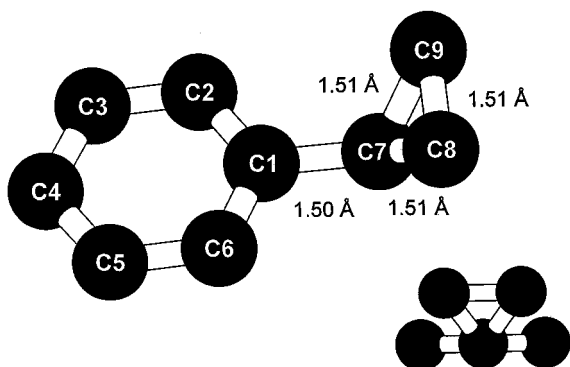
**Table 2. Experimental and calculated wavenumbers ( $\bar{\nu}$ ) of vibrations of  $1a^{+\bullet}$  and  $1b^{+\bullet}$** 

$1a^{+\bullet}/\text{cm}^{-1}$		$1b^{+\bullet}/\text{cm}^{-1}$		Possible assignment <sup>c</sup>
Expt. <sup>a</sup>	Calc. <sup>b</sup>	Expt. <sup>a</sup>	Calc. <sup>b</sup>	
		449	439	cp C <sub>7</sub> —C <sub>8</sub> str
543	550			Ph 1, Ph—cp bend
		820	837	cp C <sub>7</sub> —C <sub>8</sub> str, C <sub>8</sub> —C <sub>9</sub> str, cp—CH <sub>3</sub> str
970	992			Ph 12, cp CH <sub>2</sub> rock
		971	998	cp C <sub>7</sub> —C <sub>8</sub> + C <sub>7</sub> —C <sub>9</sub> str
1004	1007	1005	1001	Ph 12, cp CH <sub>2</sub> rock
1102	1118	1090	1118	Ph 18b
		1180	1202	cp—CH <sub>3</sub> str
1188	1177			Ph 9a
1236	1213	1234	1211	Ph 9a, cp C <sub>8</sub> —C <sub>9</sub> str [cp C <sub>7</sub> —C <sub>8</sub> str]
1336	1382	1331	1376	Ph 14
1483	1501	1488	1518	Ph 19a, Ph—cp str, cp—CH <sub>3</sub> str
1596	1645	1582	1629	Ph 8a

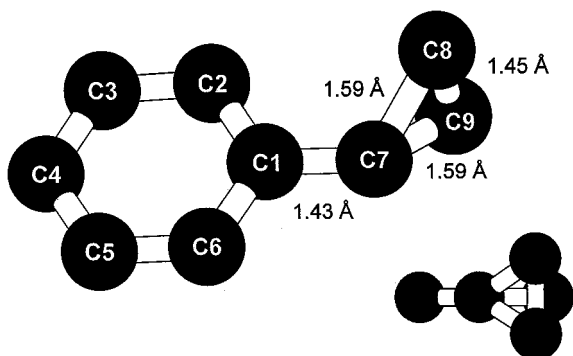
<sup>a</sup> Pump-probe resonance Raman wavenumber in acetonitrile.

<sup>b</sup> Unscaled wavenumber from DFT calculation [B3LYP functional, 6-311G(d,p) basis].

<sup>c</sup> See footnote c of Table 1. Atoms are numbered as in Figs 9 and 11.

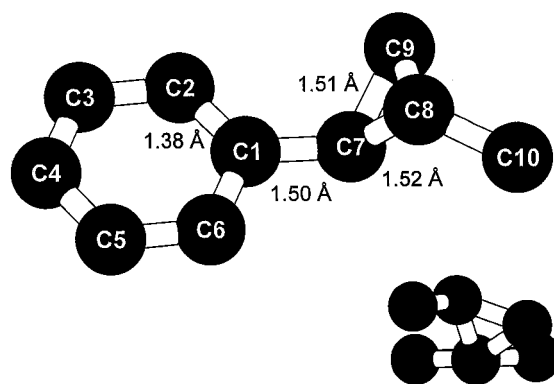


**Figure 8.** Calculated [B3LYP density functional, 6-311G(d,p) basis] equilibrium geometry (carbon atoms only) of  $1a$ . The inset shows the geometry looking down the C<sub>7</sub>—C<sub>1</sub>—C<sub>4</sub> axis with the phenyl ring in the horizontal plane. The C—C bond lengths that change significantly upon oxidation are indicated.

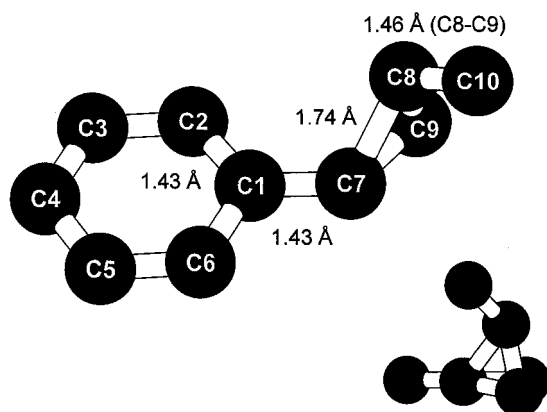


**Figure 9.** Same as Fig. 8, for  $1a^{+\bullet}$ .

resonance Raman spectroscopy to study photogenerated radical cations. Pump-probe transient resonance Raman, with a long pump-probe delay as employed here, interrogates the 'relaxed' radical cations. They have had enough time to cool vibrationally and, in all likelihood, conformationally equilibrate following their formation by electron transfer to the photoexcited sensitizer, and they



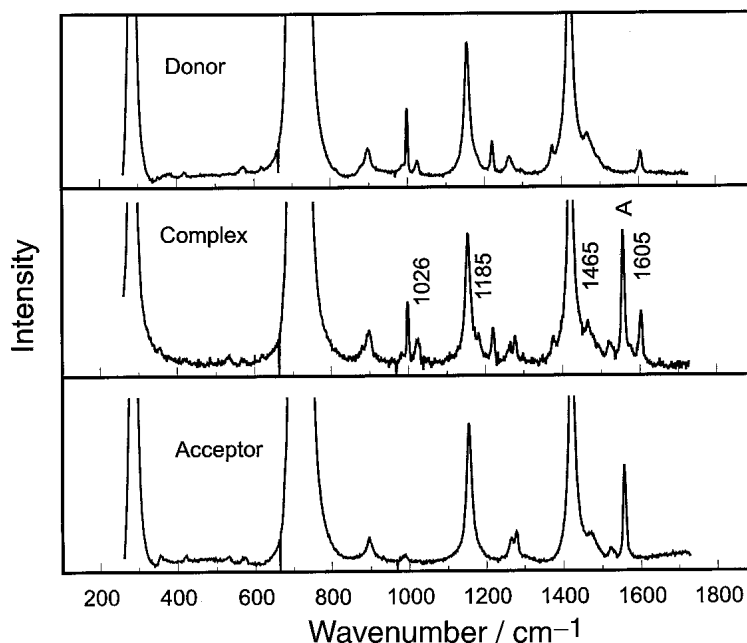
**Figure 10.** Same as Fig. 8, for  $1b$ .



**Figure 11.** Same as Fig. 8, for  $1b^{+\bullet}$ .

are presumably not ion-paired in acetonitrile, a highly polar solvent. The structural information is contained in the *vibrational wavenumbers* of the transient species. Alternatively, the *intensities* of the Raman lines of a donor-acceptor complex, obtained on resonance with a charge-transfer transition, also depend on the structure of the radical ions formed, but this information pertains to the *vertical* excited state at geometries not far from the equilibrium structure of the neutral ground-state complex.<sup>36</sup> The resonance Raman intensities of the *p*-methoxybenzyltrimethylsilane:TCNE complex imply that the geometry changes accompanying vertical charge-transfer excitation are predominantly localized on the phenyl ring.<sup>7</sup> Although we were not able to perform a corresponding quantitative analysis of the  $1a$ :TCNE complex because of the weakness of its resonance Raman spectrum, the qualitative appearance of enhancement mainly in phenyl-localized modes suggests that charge-transfer excitation initially moves the electron mainly from the phenyl group. A subsequent electronic non-adiabatic transition, solvent reorganization, ion-pair separation and/or slow conformational change such as internal rotation may then cause the positive charge to migrate partially to the cyclopropyl group which becomes highly reactive in the relaxed radical cation. It should be noted, however, that the DFT calculations on the equilibrium structures of  $1a^{+\bullet}$  and  $1b^{+\bullet}$  place more than half the positive charge on the phenyl group even though the cyclopropyl ring is greatly distorted from the neutral geometry.<sup>26</sup>

In a previous publication, CASSCF/CASPT2 calculations were used to predict and explain the electronic



**Figure 12.** Raman spectra (488 nm excitation) in dichloromethane of 60 mM phenylcyclopropane (donor), 60 mM phenylcyclopropane plus 60 mM TCNE (complex) and 60 mM TCNE (acceptor). Lines showing resonance enhancement in the complex spectrum are labeled with their wavenumbers (for donor-localized vibrations) or with A for the 1557  $\text{cm}^{-1}$  TCNE vibration.

spectra of  $1\mathbf{a}^{+\bullet}$  and the closely related cumene (isopropylbenzene) radical cation.<sup>37</sup> According to this analysis, the lowest-energy electronic transition in both species is essentially forbidden, and our 532 nm probe pulse is resonant with the second electronic transition of  $1\mathbf{a}^{+\bullet}$  ( $1^2A'' \rightarrow 3^2A''$ ), which involves primarily movement of an electron from the  $2a''$  orbital (doubly occupied in the ground state) to the  $4a''$  orbital (singly occupied in the ground state). These orbitals are localized mainly on  $C_7-C_8$  and  $C_7-C_9$  of the cyclopropyl group (atom numbering as in Fig. 9) and on  $C_1-C_2$  of the phenyl group (the bond *cis* to the cyclopropyl ring), respectively, so 532 nm excitation should generate the largest geometry changes in these bonds, and vibrations involving these bonds are the ones that should appear with highest intensity in our pump-probe spectra. Our Raman data and assignments

do not particularly bear out these expectations. Modes assignable to cyclopropyl  $C_7-C_8$  and  $C_7-C_9$  stretching seem notably absent from the resonance Raman spectrum of  $1\mathbf{a}^{+\bullet}$ , and while the phenyl  $C_1-C_2$  stretch makes a large contribution to some of the stronger lines assigned to phenyl-localized modes, it also contributes to modes that evidently do not appear in the Raman spectrum. The origin of this apparent discrepancy remains to be investigated.

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