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Time-resolved resonance Raman and density functional study of the radical cations of chlorobiphenyls

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Abstract

We have obtained time-resolved resonance Raman spectra of the radical cations of 4-chlorobiphenyl, 3-chlorobiphenyl, and 2-chlorobiphenyl. We have performed density functional theory B3LYP/6-31G^{**} calculations to find the optimized structures and predicted vibrational spectra for the ground states of the chlorobiphenyl radical cations. The computational and experimental results suggest that all of these chlorobiphenyl radical cations are nonplanar. The 2-chlorobiphenyl radical cation is noticeably more nonplanar than the other two radical cations and this appears to be due mainly to steric interactions. The radical cations are more noticeably nonplanar than the corresponding T₁ states of the neutral molecules.
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1. Introduction

Polyhalogenated biphenyls such as polychlorobiphenyls (PCBs) and polybromobiphenyls (PBBs) have been used as organic diluents, flame retardants, and plasticizers in a variety of industrial applications [1]. These compounds have varying degrees of toxicity depending on the type of halogen atom, the number and substitution pattern of the halogen atoms [2–5]. Since some PCBs and PBBs can absorb in the sunlight region [6], there have been a number of photochemical studies done for these compounds to examine the mechanism(s) of dehalogenation [7–12].

SCF–MO calculations [13] indicated that the greater the barrier height to rotation about the center carbon–carbon bond between the two phenyl groups for a congener, the lower the toxicity for that molecule. AM1 (Austin Model 1) computations for several polyhalogenated biphenyls showed that those with no *ortho*-position substitution have a planar quinoidal like structure for the T₁ state but those with four halogen atoms in the *ortho* position (2,2',-3,3',-6,6'-hexahalobiphenyls) were nonplanar in the T₁ state [14]. The planar and nonplanar T₁ states for the polyhalogenated exhibited noticeably different excitation energies [14]. We recently examined the T₁ state of 4-chlorobiphenyl, 3-chlorobiphenyl, and 2-chlorobiphenyl using time-resolved Raman spectroscopy and ab initio (CIS) calculations [15], and found that 2-chlorobiphenyl has a nonplanar structure in its T₁ state while the 3-chlorobiphenyl and 4-chlorobiphenyl T₁ states have a planar quinoidal

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structure. The twisting of the T_1 state of 2-chlorobiphenyl is likely due to an electron withdrawing effect of the *ortho*-substituted halogen atom [15] since EPR experiments for methylbiphenyls indicate that 2-methylbiphenyl has a planar quinoidal structure [16].

The optical and kinetics properties of a number of monohalogenated biphenyls and polyhalogenated biphenyls have been examined in a series of pulse radiolysis experiments [17,18]. Comparison of these results with data from photoelectron spectroscopy experiments [19] suggests that the monohalogenated biphenyls undergo some degree of planarization upon production of their respective radical cations. We have recently used time-resolved resonance Raman spectroscopy to directly probe the radical cation of 4,4'-dibromobiphenyl [20] structure and our results indicated that its radical cation has a planar or nearly planar structure similar to the radical cation of biphenyl [21–27].

In this Letter, we report the first (to our knowledge) resonance Raman spectra of the radical cations of 2-chlorobiphenyl, 3-chlorobiphenyl, and 4-chlorobiphenyl. We have also done density functional theory (DFT) calculations to help characterize the structures of these radical cations and make vibrational assignments to the experimentally observed Raman bands. We discuss the effect of the chlorine atom substitution position on the structures of the radical cations of the chlorobiphenyls and compare their structures to the T_1 states of the chlorobiphenyls.

2. Experimental

The experimental apparatus and methods used for the nanosecond time-resolved resonance Raman experiments have been reported previously so only a short description will be presented here [15,20, 28–30]. The resonance Raman experiments used samples 4-chlorobiphenyl (5–10 mM), 3-chlorobiphenyl (5–10 mM), and 2-chlorobiphenyl (65 mM) prepared with spectroscopic grade acetonitrile solvent. The harmonics of a nanosecond Nd:YAG laser and their hydrogen Raman shifted laser lines were used for pump and probe excitation wavelengths (274 nm pump and 416 nm probe for 4-chlorobiphenyl; 266 nm pump and 369 nm probe for 3-chlo-

robiphenyl and 2-chlorobiphenyl). An optical delay was used to set the time-difference between the pump and probe laser beams. A near-collinear geometry was used to loosely focus the pump and probe laser beams onto a flowing liquid stream of sample. A backscattering excitation and collection geometry was used and an ellipsoidal mirror collected the Raman light and imaged it through a depolarizer and entrance slit of a 0.5 m spectrograph. A 1200 groove/mm grating dispersed the Raman light onto a liquid-nitrogen-cooled CCD mounted on the exit port of the spectrograph. The CCD detector collected the Raman signal for $\sim 60 \times 15$ s scans and then readout the accumulated signal to an interfaced PC computer. Ten to twenty of these readouts were added together to get a Raman spectrum. Probe only scans, pump only scans, and background scans were appropriately scaled and subtracted from the pump plus probe scans to obtain the transient resonance Raman spectrum. The Raman shifts of the spectra were calibrated using the known vibrational frequencies of the acetonitrile solvent bands. Scans of an intensity calibrated tungsten lamp were used to correct the spectra for the wavelength variation of the detection system.

3. Calculations

DFT calculations of the structures and the vibrational frequencies of the neutral molecule and radical cations of 4-chlorobiphenyl, 3-chlorobiphenyl, and 2-chlorobiphenyl were done using the GAUSSIAN program suites (G94 run on an IBM 9076 SP2 computer and G98W run on a PC computer) [31]. The DFT computations employed Becke's three-parameter hybrid method with the Lee–Yang–Parr correlation functional (abbreviated as B3LYP) and the 6-31G** split valence plus polarization basis set [32]. The gradients and vibrational frequencies were found analytically and no imaginary frequency modes were observed at the optimized structures for all of the species investigated. The vibrational mode descriptions were determined using the potential energy distributions (PED) obtained from the program NMODES [33] and visual inspection of the normal modes animated using the MOLDEN program [34]. The calculated vibrational frequencies were scaled by

0.976. The root mean square deviation of the scaled B3LYP/6-31G^{**} vibrational frequencies from the experimental frequencies was $\sim 10 \text{ cm}^{-1}$.

4. Results and discussion

Table 1 shows the optimized structural parameters found from the B3LYP/6-31G^{**} computations for the neutral molecules and radical cations of 4-chlorobiphenyl, 3-chlorobiphenyl, and 2-chlorobiphenyl as well as results from B3LYP/6-31G^{*} calculations by Tasumi and co-workers [35] for the radical cation of biphenyl. The numbering of the atoms used in Table 1 for the chlorobiphenyls is illustrated in Fig. 1 for 4-chlorobiphenyl. The computed structures of the neutral molecule and radical cation of 4-chlorobiphenyl and 3-chlorobiphenyl in their ground states are very similar to one another and to the corre-

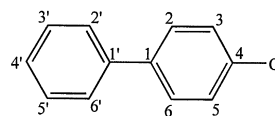


Fig. 1. Schematic diagram of 4-chlorobiphenyl with the atoms numbered. The numbering system for the biphenyl carbon atoms and hydrogen atoms is the same for 3-chlorobiphenyl, 2-chlorobiphenyl, 2-methylbiphenyl, and biphenyl. This numbering scheme is used for the structural parameters of all the molecules and radical cations in Table 1.

sponding species of biphenyl: the S_0 neutral molecules are twisted $\sim 38^\circ$ between the two phenyl rings while the S_0 radical cations are twisted $\sim 20^\circ$ between the two phenyl rings. In contrast, the computed structure for 2-chlorobiphenyl is significantly different from those for 4-chlorobiphenyl, 3-chlorobiphenyl, and biphenyl. 2-Chlorobiphenyl has a twist angle between the two phenyl rings of $\sim 56^\circ$ for the

Table 1

Structural parameters for the ground state of the neutral molecules and radical cations of 4-chlorobiphenyl (4CBP), 3-chlorobiphenyl (3CBP), 2-chlorobiphenyl (2CBP), 2-methylbiphenyl (2MBP), and biphenyl (BP) calculated using B3LYP density functional theory A 6-31G^{**} basis set was used to compute the 4CBP, 3-CBP, 2-CBP, and 2-MBP results. The BP results are from Ref. [35] (B3LYP/6-31G^{*} calculations). S_0 = ground state of neutral molecule and RC = ground state of radical cation

Parameters	4CBP		3CBP		2CBP		2MBP		BP ^a	
	S_0	RC	S_0	RC	S_0	RC	S_0	RC	S_0	RC
Twist angle between two phenyl rings ($^\circ$)	38.3	19.7	38.6	20	55.9	36.8	53.5	33.6	38.3	19.5
C_1-C_1' (\AA)	1.485	1.446	1.486	1.447	1.4896	1.448	1.492	1.448	1.486	1.444
C-Cl	1.759	1.712	1.762	1.729	1.764	1.731	—	—	—	—
C_1-C_2	1.405	1.431	1.405	1.421	1.406	1.445	1.414	1.453	1.405	1.433
C_2-C_3	1.393	1.376	1.392	1.381	1.395	1.391	1.402	1.392	1.394	1.379
C_3-C_4	1.394	1.413	1.394	1.418	1.393	1.394	1.394	1.399	1.396	1.403
C_4-C_5	1.394	1.413	1.395	1.400	1.395	1.412	1.394	1.412	1.396	1.403
C_5-C_6	1.393	1.376	1.393	1.382	1.392	1.377	1.393	1.374	1.394	1.379
C_6-C_1	1.405	1.431	1.405	1.436	1.406	1.428	1.405	1.434	1.405	1.433
C_2-H_2	1.086	1.083	1.084	1.082	—	—	1.514 ^b	1.507 ^b	1.087	1.083
C_3-H_3	1.084	1.084	—	—	1.084	1.084	1.088	1.085	1.087	1.085
C_4-H_4	—	—	1.084	1.085	1.086	1.085	1.087	1.086	1.087	1.086
$C_2C_1C_1'$ ($^\circ$)	121.1	121.2	120.4	121.1	124.4	124.5	122.7	123.7	—	—
$C_2C_1C_6$	117.8	117.5	118.5	118.3	116.7	116.8	119.1	118.6	118.1	117.8
$C_1C_2C_3$	121.4	121.5	120.0	120.2	121.8	121.1	118.5	117.9	121.0	120.9
$C_2C_3C_4$	119.2	119.3	121.7	120.8	120.0	119.9	121.9	122.0	120.3	120.0
$C_3C_4C_5$	120.9	120.8	118.4	119.7	119.7	120.6	119.5	120.5	119.4	120.4
$C_1C_2H_2(\text{Cl})$	119.5	120.0	120.4	120.8	121.1	121.4	122.6	123.8	119.4	120.0
$C_2C_3H_3(\text{Cl})$	120.7	121.0	119.1	120.5	119.3	119.5	118.7	118.9	119.6	120.1
$C_3C_4H_4(\text{Cl})$	119.6	119.6	120.3	119.4	119.6	119.4	120.0	119.6	120.3	119.8

^aValues are from Ref. [35].

^bThis is a C–C bond length for 2MBP.

neutral molecule S_0 state and $\sim 37^\circ$ for the radical cation in its ground state. In order to help assess the relative importance of steric effects vs. 2-position electron withdrawing effects, we have also done corresponding B3LYP/6-31G** calculations for the 2-methylbiphenyl system (results in Table 1) since the chlorine atom is no more demanding sterically than the methyl group [16]. 2-Methylbiphenyl has a twist angle between the two phenyl rings of $\sim 53.5^\circ$ for the neutral molecule S_0 state and $\sim 33.6^\circ$ for the radical cation in its ground state. Comparison of the computed structural parameters of 2-chlorobiphenyl and 2-methyl biphenyl in Table 1 indicates that the additional twisting found for 2-chlorobiphenyl compared to the 3-chlorobiphenyl and 4-chlorobiphenyl neutral molecules and radical cations in their ground states is mainly due to steric interactions. There is possibly some additional twisting (probably on the order of several degrees) due to electron withdrawal effects of the chlorine atom at the 2-position. The bond lengths shown in Table 1 for the interring $C_1-C'_1$ and C–Cl bonds become shorter upon formation of the radical cations from the corresponding neutral molecules whereas the C_1-C_2 bond becomes longer. The change in the interring $C_1-C'_1$ bond length upon formation of the radical cation from the neutral molecule is -0.039 Å for 4-chlorobiphenyl and 3-chlorobiphenyl, and -0.042 Å for 2-chlorobiphenyl. This appears to correlate with the change in the twisting angle upon formation of the radical cation from the neutral molecule (a change of 17.6° for 4-chlorobiphenyl and 3-chlorobiphenyl, and 19.1° for 2-chlorobiphenyl).

It is interesting to compare our calculated results for the radical cations of the chlorobiphenyls with those previously found for the corresponding T_1 triplet states [15]. The T_1 triplet states of 4-chlorobiphenyl and 3-chlorobiphenyl were computed to be planar in structure while the 2-chlorobiphenyl T_1 state was calculated to be twisted by $\sim 29^\circ$ (for CIS/6-31G(d) split valence plus polarization basis set computations). This is in contrast to the radical cations of the chlorobiphenyls which were all computed to have a nonplanar structure (although to varying degrees). The change from a neutral system to a radical cation appears to decrease the degree of planarity but not to the extent found for the corresponding neutral triplet state molecules. This is con-

sistent with experimental work that suggest that formation of the radical cation from the neutral molecule for halobiphenyls undergoes at least partial planarization (although these studies did not put a quantitative amount) [17–19]. The C–Cl bond becomes noticeably weaker in the T_1 state of the neutral chlorobiphenyls (e.g., the bond lengthens by ~ 0.06 – 0.07 Å) but becomes stronger in the ground state radical cations (e.g., the bond decreases by ~ 0.03 – 0.05 Å) compared to the S_0 ground state of the neutral molecule. This suggests that it would be somewhat easier to cleave the C–Cl bond of the T_1 state of the neutral molecule compared to the ground state of the radical cations (possibly by further excitation via an excimer and/or electron transfer reaction mechanism).

Fig. 2 presents the time-resolved resonance Raman spectra of the radical cations of 4-chlorobiphenyl, 3-chlorobiphenyl, and 2-chlorobiphenyl in acetonitrile solution. The optical delay between the probe and pump laser pulses is ~ 15 ns. Transient resonance Raman spectra of 4,4-dibromobiphenyl triplet state and radical cation in polar solvents such as acetonitrile [20] indicated the radical cation is formed by a multiphoton process (most likely a two-photon process). A similar result for biphenyl radical cation was also reported by Buntinx and co-workers [25]. The spectrum of the 4-chlorobiphenyl radical cation in Fig. 2 was obtained by subtraction of an appropriately scaled time-resolved resonance Raman spectrum of 4-chlorobiphenyl in acetonitrile with 0.12 M diethylamine added in which the radical cation is completely quenched and only T_1 bands remain (e.g., the T_1 spectrum) from the time-resolved resonance Raman spectrum of 4-chlorobiphenyl in acetonitrile (e.g., the radical cation plus T_1 spectrum). Due to the relatively low signal-to-noise spectra that could be obtained for the time-resolved resonance Raman spectra of 3-chlorobiphenyl and 2-chlorobiphenyl, this subtraction was not done and Fig. 2 shows both radical cation and T_1 bands in these spectra. The triplet state and radical cations of halobiphenyls have substantially different lifetimes and their vibrational signals can be distinguished by the pump–probe delay dependence of the resonance Raman bands [30]. Since it was not practical to introduce an optical delay of > 30 ns in our laboratory and we do not have the equipment to set

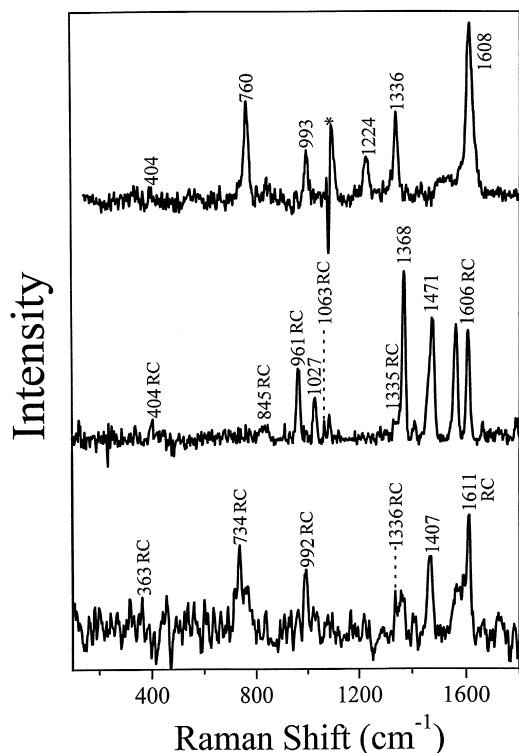


Fig. 2. Nanosecond time-resolved resonance Raman spectra of the radical cations of: 4-chlorobiphenyl (top), 3-chlorobiphenyl (middle), and 2-chlorobiphenyl (bottom). The 4-chlorobiphenyl spectrum has had the triplet state spectrum removed but the 3-chlorobiphenyl and 2-chlorobiphenyl spectra contain both radical cation and triplet state Raman bands. The Raman shifts (in cm^{-1}) of some of the Raman bands are marked and RC indicates radical cation bands in the 3-chlorobiphenyl and 2-chlorobiphenyl spectra.

up an appropriate electronic delay between the pump and probe pulses, the radical cation resonance Raman bands were assigned by making use of the T_1 only spectra previously reported for monochlorobiphenyls [15]. Table 2 presents a comparison of the calculated and experimental vibrational frequencies of the ground state neutral molecules and radical cations of 4-chlorobiphenyl, 3-chlorobiphenyl, and 2-chlorobiphenyl, respectively. There is generally reasonable agreement between the calculated and experimental vibrational frequencies for the preliminary vibrational assignments shown in Table 2.

Examination of the nominal interring stretch mode, ν_6 , shows some interesting trends upon going from the neutral molecule to the radical cation in the

chlorobiphenyls. The calculated and experimental vibrational frequencies for the interring stretch ν_6 mode are 1280 and 1287 cm^{-1} for the S_0 state of the neutral 4-chlorobiphenyl molecule and 1325 and 1334 cm^{-1} for the ground state radical cation 4-chlorobiphenyl, respectively. The change in vibrational frequency for the ν_6 interring mode upon formation of the radical cation from the neutral 4-chlorobiphenyl molecule is $+44 \text{ cm}^{-1}$ for the computed frequencies and $+47 \text{ cm}^{-1}$ for the experimental frequencies. Inspection of Table 2 shows that the corresponding changes in the ν_6 interring mode is similar for 3-chlorobiphenyl ($+44 \text{ cm}^{-1}$ for computed frequencies or $+54 \text{ cm}^{-1}$ for the experimental frequencies) and biphenyl ($+60 \text{ cm}^{-1}$ experimental frequencies or $+42 \text{ cm}^{-1}$ calculated frequencies) but somewhat smaller for the 2-chlorobiphenyl system ($+36 \text{ cm}^{-1}$ for computed frequencies and $+38 \text{ cm}^{-1}$ for the experimental frequencies). This is consistent with the B3LYP DFT results that indicate the biphenyl, 4-chlorobiphenyl and 3-chlorobiphenyl neutral molecules and radical cations have very similar twist angles between the two phenyl rings. In contrast, the smaller increases in the ν_6 interring vibrational frequency upon formation of the radical cation from the neutral molecule for 2-chlorobiphenyl suggest that 2-chlorobiphenyl radical cation does not undergo as much partial planarization as the 4-chlorobiphenyl, 3-chlorobiphenyl, and biphenyl radical cations. This is also consistent with the calculated structural changes of Table 1.

It is interesting to compare the change in vibrational frequency for the ν_6 interring mode of the radical cation to that of the T_1 state after formation from the neutral molecule. The changes in frequency are noticeably greater for the T_1 state (experimental frequencies changes are $\Delta\nu = +79 \text{ cm}^{-1}$ for 4-chlorobiphenyl, $+88 \text{ cm}^{-1}$ for 3-chlorobiphenyl, and $+65 \text{ cm}^{-1}$ for 2-chlorobiphenyl) [15] than for the radical cations (experimental frequencies changes are $\Delta\nu = +47 \text{ cm}^{-1}$ for 4-chlorobiphenyl, $+54 \text{ cm}^{-1}$ for 3-chlorobiphenyl, and $+38 \text{ cm}^{-1}$ for 2-chlorobiphenyl). This indicates a greater degree of planarization in the triplet states than in the radical cations and is consistent with the results of the B3LYP (reported here) and CIS [15] calculations. EPR experiments for the T_1 states of 4-methylbiphenyl, 3-methylbiphenyl, and 2-methylbiphenyl indicate that they

Table 2

Comparison of experimental vibrational frequencies with computed values for the ground states of 4-chlorobiphenyl, 3-chlorobiphenyl and 2-chlorobiphenyl neutral molecules and their radical cations

(o.p.) = out of plane, def. = deformation. Raman intensity descriptions: vw = very weak, w = weak, m = medium, s = strong, vs = very strong

Approx. description	Neutral molecule		Radical cation	
	expt. ^a	calc. ^b	expt. ^c	calc. ^b
<i>(A) 4-Chlorobiphenyl:</i>				
Interring def.	112 m	99		116
C–Cl bend (o.p.) + ring def. (o.p.)	189 vw	178		160
C–Cl bend or stretch	262 m	261		265
Interring def., ν_{14}	332 w	327	335 vw?	304
Ring def. (o.p.), ν_{13}	411 w	414	401 vw?	389
C–Cl stretch	478 vw	468		483
Ring def. (o.p.)	545 vw	543		
Interring def.	617 w	616		
interring def.	636 vw	633		
Ring def.	662 vw	656		658
Ring breath, ν_{12}	764 s	757	762 s	756
C–H def. (o.p.)	827 vw	822		794
C–H def. (o.p.), ν_{11}	838 vw	840		811
C–H def. (o.p.), ν_{10}	967 vw	910	844 w	840
Ring breathing, ν_9	998 s	996	993 s	965
C–H def.	1016 vw	1014		
C–H def., ν_8	1041 w	1042		
C–H def.	1096 s	1084		1092
C–H def.	1160 w	1159		1163
C–H def., ν_7	1188 w	1187	1224 s	1190
Interring C–C stretch, ν_6	1287 vs	1280	1334 s	1325
C–H def.	1451 vw	1454		1458
Ring C–C stretch, ν_5	1507 m	1511	1510 vw	1494
Ring C–C stretch, ν_4	1603 vs	1620	1608 vs	1622
<i>(B) 3-Chlorobiphenyl:</i>				
Interring def.	109 m	101		117
C–Cl bend (o.p.) + ring def. (o.p.)	201 m	191		
C–Cl def.	234 m	225		
Interring def.	284 m	277		
Interring def. (o.p.), ν_{14}	324 w	314	337 vw?	327
Interring def.	380 vw	377	404 w?	394
Ring def. (o.p.), ν_{13}	422 vw	412		
C–Cl stretch	450 vw	448		
Ring def.	582 vw	579		536
Ring def.	612 vw	611		
Ring breath	685 m	678		670
C–H def. (o.p.), ν_{12}	797 w	784		
C–H def. (o.p.), ν_{11}	844 vw	840	845 vw	872
C–H def. (o.p.), ν_{10}	972 vw	913		
Ring breathing, ν_9	1001 vs	991	961 s	963
C–H def., ν_8	1023 vw	1018	1063 m	1074
C–H def.	1084 vw	1080		
C–H def.	1160 w	1168		1099
C–H def., ν_7	1184 vw	1183		1160
C–H def.	1256 m	1262		1201

Table 2 (continued)

Approx. description	Neutral molecule		Radical cation	
	expt. ^a	calc. ^b	expt. ^c	calc. ^b
<i>(B) 3-Chlorobiphenyl:</i>				
Interring C–C stretch, ν_6	1281 vs	1277	1335 w	1321
C–H def.	1306 m	1315		
Ring C–C stretch	1454 vw	1456		1439
Ring C–C stretch, ν_5	1505 w	1507		1484
Ring C–C stretch	1592 vw	1592		
Ring CC stretch, ν_4	1601 vs	1619	1606 vs	1613
<i>(C) 2-Chlorobiphenyl:</i>				
Interring def.	116 s	96		110
Interring def.	186 m	173		175
C–Cl def.	230 m	223		229
Interring def.	285 w	279		259
Interring def. (o.p.), ν_{14}	316 w	309	313 vw?	301
Interring def.	388 vw	386		
Ring def. (o.p.), ν_{13}	407 vw	407	363 vw?	386
C–Cl stretch	434 s	424		
Ring def. (o.p.)	463 w	460		495
Ring def. (o.p.)	534 vw	528		
Ring def. (o.p.)	557 vw	553		
Interring def.	618 m	618		
Ring breath, ν_{12}	683 s	673		665
C–H def. (o.p.)	762 w	767	734 s	744
C–H def. (o.p.), ν_{11}	847 vw	841	837 w	815
C–H def. (o.p.), ν_{10}	917 vw	911		946
Ring breathing, ν_9	1000 vs	996	992 s	960
Ring def., ν_8	1036 vs	1030		985
C–H def.	1130 w	1124		1140
C–H def.	1161 m	1159		
C–H def., ν_7	1184 w	1181	1165 w	1166
Ring C–C stretch	1248 m	1268		1280
Interring C–C stretch, ν_6	1298 vs	1300	1336 m	1336
C–H def.	1450 vw	1454		
Ring C–C stretch, ν_5	1501 m	1506		1477
Ring C–C stretch	1568 w	1574		1508
Ring C–C stretch, ν_4	1601 vs	1620	1611 vs	1610

^a Values from FT–Raman spectra of Ref. [15]. Estimated uncertainties of FT–Raman vibrational frequencies is $\pm 2 \text{ cm}^{-1}$.

^b Values from B3LYP/6-31G** calculations (see text for more details).

^c Values from time-resolved resonance Raman spectra of Fig. 2. Estimated uncertainties of Raman vibrational frequencies is $\pm 4 \text{ cm}^{-1}$.

are planar [16]. Comparison with our previous results for the T_1 states of the monochlorobiphenyls could suggest the increased twisting of the 2-chlorobiphenyl T_1 state is mainly due to electron withdrawal effects [15]. This is in contrast to our present results for the radical cations of chlorobiphenyls which suggest that the additional twisting of the 2-chlorobi-

phenyl radical cation relative to the 4-chlorobiphenyl and 3-chlorobiphenyl radical cations is mainly due to steric effects although there are probably some moderate 2-position (*ortho*) electron withdrawal effects present. We note the caveat that the EPR methylbiphenyl results were obtained in 77 K glasses [16] and not in the solution phase. It is not clear if the

solvent significantly affects the 2-position electron withdrawal effect in the triplet states or radical cations and further work with differing solvents is needed to address this issue. It would appear useful to perform a series of solution-phase T_1 resonance Raman experiments and ab initio calculations for fluoro, chloro, and bromo monohalo substituted biphenyl compounds in order to better evaluate the relative importance of steric vs. 2-position electron withdrawing effects in solution-phase triplet states.

We observe some very weak features in the chlorobiphenyl radical cation spectra in the 360–400 cm^{-1} region (see Fig. 2) that can be tentatively assigned to the out-of-plane ring deformation ν_{13} mode (401 cm^{-1} in 4-chlorobiphenyl, 404 cm^{-1} in 3-chlorobiphenyl, and 363 cm^{-1} in 2-chlorobiphenyl). These bands have very low signal to noise (the fluorescence/phosphorescent background limited our resonance Raman detection) and are somewhat uncertain. A similar very weak band at 391 cm^{-1} was observed in radical cation spectra of biphenyl [22]. This 391 cm^{-1} band was tentatively assigned to the ν_{13} mode and used to suggest that the radical cation of biphenyl has a slightly twisted structure between the two phenyl rings [22]. One could use a similar reasoning to suggest that the radical cations of 4-chlorobiphenyl, 3-chlorobiphenyl, and 2-chlorobiphenyl are nonplanar. This would be consistent with the DFT calculation results presented here. However, better signal-to-noise resonance Raman spectra of the radical cations are needed to ascertain if this is actually the case. It should be possible to acquire better signal-to-noise resonance Raman spectra of the radical cations of these chlorobiphenyls by using a gated ICCD detector (this is not currently available to us) to better discriminate the probe resonance Raman signal from the fluorescence/phosphorescent background.

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