Transient Resonance Raman Investigation of 4-Iminocyclohexa-2,5-dienylidene and 4-Oxocyclohexa-2,5-dienylidene Carbenes in Aqueous Solution

Wing Sum Chan, King Hung Leung, Shing Yau Ong, and David Lee Phillips*

Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong S.A.R., P. R. China

Received: November 19, 2001; In Final Form: April 19, 2002

We present transient resonance Raman spectra for the 4-iminocyclohexa-dienylidene and 4-oxocyclohexa-2,5-dienylidene carbene species in aqueous solutions. Comparison of the experimental vibrational frequencies to values computed from density functional theory calculations suggests that both carbenes are in their triplet states. Comparison of the structure and properties of the 4-iminocyclohexa-dienylidene to those previously found for several arylnitrenium ions indicates that the imine and cyclohexadienyl character of the 4-iminocyclohexa-2,5-dienylidene carbene is similar to the diphenylnitrenium ion. This suggests the smaller C−N bond order and lower cyclohexadienyl character of the triplet 4-iminocyclohexa-2,5-dienylidene carbene compared to the higher C═O bond order and greater cyclohexadienyl character of the triplet 4-oxocyclohexa-2,5-dienylidene carbene is mainly due to the charge delocalization ability of the second hydrogen atom in the $-NH_2^+$ moiety. We briefly discuss the structure and properties of these two carbenes and their similarities and differences in chemical reactivity.

Introduction

The photochemistry of haloaromatic compounds is of interest from both synthetic[1−8] and environmental[10−23] viewpoints. Ultraviolet excitation of arylhalides can result in homolytic carbon−halogen bond cleavage and can be subsequently used to synthesize a variety of substances.[1,2] Ultraviolet excitation of aryl halides under some conditions can undergo heterolytic C−X bond cleavage to give nucleophilic photosubstitution reactions.[3−8] This competition between homolytic and heterolytic C−X bond cleavage processes is also observed for alkyl halide photochemistry.[9] Aryl halides are used in a number of applications and can be found in the environment as pollutants. Examples include polychlorinated biphenyls (PCBs),[10−15] polybrominated biphenyls (PBBs),[10−15] halophenols,[16−20] haloanilines,[21−23] and others. Photodegradation of these aryl halides can potentially play an important part in removal of these impurities from natural waters.

Nanosecond transient absorption spectroscopy experiments have been done to elucidate the intermediates and reaction mechanism(s) involved in the ultraviolet photolysis of 4-chlorophenol in room-temperature aqueous solutions and several other solvents.[24] This work observed a transient absorption at the end of the photolysis laser pulse that had absorption maxima at ∼384 and 370 nm in aqueous solution that was attributed to the 4-oxocyclohexa-2,5-dienylidene carbene species formed after HCl elimination from the photoexcited 4-chlorophenol.[24] This species was produced with a high quantum yield (about 0.75) in neutral and acidic aqueous solutions and enabled a thorough study of the kinetics and reactions of a carbene in an aqueous solution to be done for the first time.[24] The 4-oxocyclohexa-2,5-dienylidene carbene species had been previously observed in low-temperature matrixes.[25−27] Matrix isolation and transient absorption spectroscopy in liquids indicate that this carbene readily reacts with oxygen to form *p*-benzoquinone O-oxide[28,29] and ESR experiments also indicate the carbene is in the triplet state.[30,31] A more recent study investigated the photochemistry of 4-chloroaniline in aqueous solution using transient absorption spectroscopy and product analysis.[32] This study reported the first spectroscopic observation of the 4-iminocyclohexa-dienylidene carbene species and observed that, although its chemical reactivity was similar to that of 4-oxocyclohexa-2,5-dienylidene carbene, there were several significant differences.[24,32] For example, photolysis of 4-chloroaniline is able to produce the 4-iminocyclohexa-dienylidene carbene species in nonprotic polar solvents such as acetonitrile, whereas the 4-oxocyclohexa-2,5-dienylidene carbene species was not produced in similar solvents after photolysis of 4-chlorophenol.[24,32] The reaction mechanisms for 4-chloro-*N*,*N*-dimethylaniline and 4-chloroaniline are the same after ultraviolet excitation to produce the carbene species although this is not the case for the corresponding derivatives for 4-chlorophenol and 4-chloroanisole.[24,32] In the presence of oxygen, 4-chloroaniline and 4-chlorophenol gave noticeably different product distributions.

In this paper, we report a transient resonance Raman spectroscopy and density functional theory investigation of the 4-iminocyclohexa-dienylidene and 4-oxocyclohexa-2,5-dienylidene carbene species in aqueous solutions. To our knowledge, these are the first time-resolved resonance Raman spectra reported for short-lived organic carbenes in aqueous solutions. We observe a number of Raman bands for each of these carbenes. Comparison of the experimental vibrational frequencies to those predicted from density functional theory calculations, indicate that both carbenes are in their triplet states. We discuss the structure and properties of these two carbenes and the similarities and differences in their chemical reactivity.

Experiment and Calculations

4-Chloroaniline (98%) and 4-chlorophenol (98%) were purchased and were further purified by steam distillation and vacuum sublimation, respectively. Samples were prepared with

---

* To whom correspondence should be addressed. E-mail: phillips@hkucc.hku.hk. Fax: 852-2857-1586.

10.1021/jp014254y CCC: $22.00

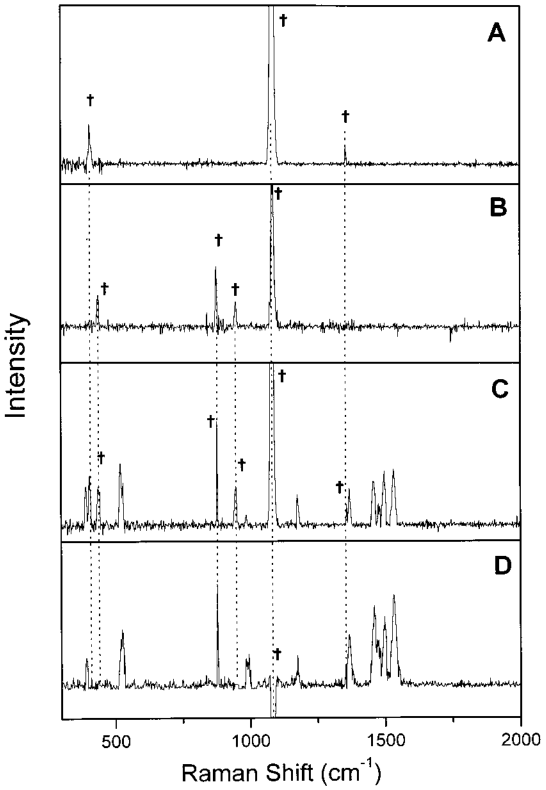

Figure 1. Probe only (A), pump only (B), pump−probe (C), and transient resonance Raman spectra (D) for 4-iminocyclohexa-dienylidene in aqueous solution. The pump and probe excitation wavelengths were 266 and 416 nm respectively. The transient Raman spectrum was obtained by subtracting the probe only spectrum and the pump only spectrum from the pump−probe spectrum. The daggers mark subtraction artifacts or scattered light artifacts.

concentrations in the 0.026−0.030 M range using distilled water. The transient resonance Raman spectra of each carbene was acquired using an experimental apparatus and methods similar to that detailed elsewhere so only a short account will be given here.[33−38] The fourth harmonic (266 nm) of a Nd:YAG laser provided the pump wavelength, and the hydrogen Raman shifted laser lines (368.9 and 416 nm) from the harmonics of a second Nd:YAG laser supplied the probe excitation wavelengths. An electronic time delay using a pulse delay generator (SRS model DG-535) was used to synchronize the pump and probe beams of the two lasers.[38] The relative timing of the pump and probe beams was measured using the signal from two fast photodiodes and a 500 MHz oscilloscope and a time delay of about 10 ns was used in the experiments.[38] A near collinear geometry was used to losely focus the pump and probe laser beams onto a flowing liquid stream of sample, and a backscattering geometry was used to collect the Raman scattered light. The Raman light was then imaged through a depolarizer and entrance slit of a 0.5 m spectrograph which dispersed the Raman light onto a liquid-nitrogen-cooled CCD detector that accumulated the Raman signal for about 300 s before being read out to an interfaced PC computer. Approximately 10−20 of these readouts were added up to obtain a Raman spectrum. Pump only, probe only, and pump−probe resonance Raman spectra were obtained, and a background scan was also acquired. The known Raman frequencies of the water solvent and parent compounds were used to calibrate the Raman shifts (cm^{-1}) of the resonance Raman spectra. The probe only and pump only spectra were subtracted from the pump−probe Raman spectrum to get the transient resonance Raman spectrum of each carbene.

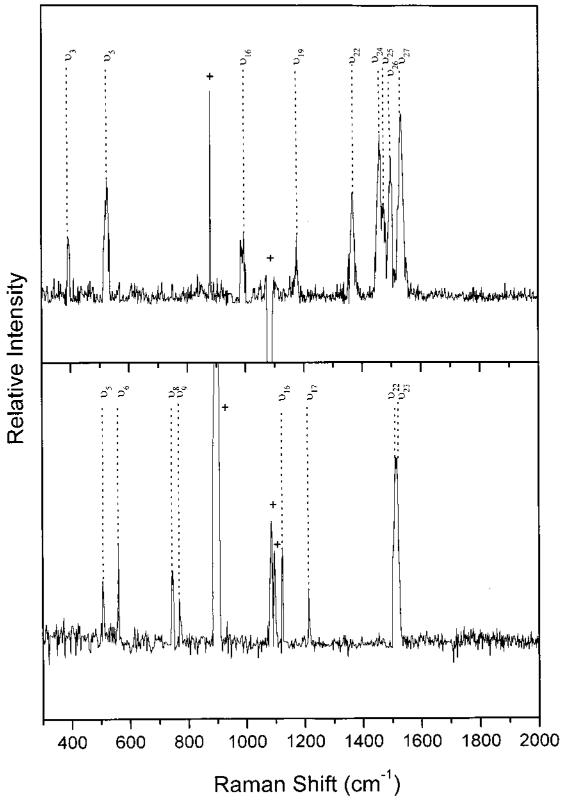

Figure 2. Transient resonance Raman spectra of 4-iminocyclohexa-dienylidene (top) and 4-oxocyclohexa-2,5-dienylidene (bottom) carbene species in aqueous solutions. The larger Raman bands are labeled with their tentative vibrational assignment, and the daggers mark subtraction artifacts or scattered light artifacts.

The Gaussian program suite was used for all of the density functional theory computations reported here.[39] Complete geometry optimization and vibrational calculations were done analytically using the UBPW91 or BPW91[40,41] methods employing the cc-PVDZ basis set[42] for the singlet and triplet states of 4-iminocyclohexa-dienylidene and 4-oxocyclohexa-2,5-dienylidene carbene species.

Results and Discussion

Photolysis of 4-chlorophenol in aqueous solution with 266 nm light results in a prompt transient absorption with maxima at 370 and 384 nm that has been assigned to the triplet state of 4-oxocyclohexa-2,5-dienylidene carbene.[24] Similarly, 266 nm photolysis of 4-chloroanailine in aqueous solution produces a transient absorption on the nanosecond time scale with maxima at 390 and 407 nm that was assigned to the 4-iminocyclohexa-2,5-dienylidene carbene.[32] We used a 266 nm pump wavelength for our transient resonance Raman experiments, a 368.9 nm probe wavelength to investigate the 4-oxocyclohexa-2,5-dienylidene carbene, and a 416 nm probe wavelength to examine the 4-iminocyclohexa-2,5-dienylidene carbene. Figure 1 displays typical probe only (A), pump only (B), pump−probe (C), and resulting transient (D) resonance Raman spectra obtained for the 4-iminocyclohexa-2,5-dienylidene carbene in aqueous solution. Figure 2 shows the transient resonance Raman spectra acquired for the 4-iminocyclohexa-2,5-dienylidene and 4-oxocyclohexa-2,5-dienylidene carbenes in aqueous solutions with the larger Raman bands labeled with their tentative vibrational assignments.

Table 1 presents the vibrational frequencies and tentative assignments for the resonance Raman bands observed in the

TABLE 1: Comparison of the Experimental Vibrational Frequencies (in cm^{-1}) Found[a]

possible assignment	singlet state BPW91/ cc-PVDZ	possible assignment	triplet state BPW91/ cc-PVDZ	experiment transient raman	experiment infrared
		4-Iminocyclohexa-dienylidene			
ν_2, ring def.	244	ν_2, ring def.	336		
ν_3, C−N bend	375	**ν_3, C−N bend**	**378**	**393**	
ν_4, ring def.	398	ν_4, ring def.	471		
ν_5, C−H+C−N bend	417	**ν_5, CCC bend**	**514**	**524**	
ν_6, C−H+C−N bend	421	ν_6, ring def. + NH_2 scissor	548		
ν_7, ring def. +NH_2 twist	516	ν_7, CCC bend	558		
ν_8, CCC bend	544	ν_8, NH_2 wag + ring def.	584		
ν_9, C−H + C−N bend	657	ν_9, ring def.	689		
ν_{10}, N−H twist +C−H bend	680	ν_{10}, C−H bend (o.p.)	754		
ν_{11}, ring def.	711	ν_{11}, ring def.	785		
ν_{12}, C−C bend (o.p.)	772	ν_{12}, ring def.	798		
ν_{13}, C−C bend + C−H bend	847	ν_{13}, ring def.	937		
ν_{14}, C−H bend (o.p.)	869	ν_{14}, ring def.	940		
ν_{15}, C−C bend + C−H bend	895	ν_{15}, ring def.	942		
ν_{16}, NH_2 rock + C−H bend	1002	**ν_{16}, C−C stretch**	**984**	**987**	
ν_{17}, C−C str. + N−H str.	1023	ν_{17}, NH_2 rock + C−C str.	1001		
ν_{18}, NH_2 rock + C−H bend	1079	ν_{18}, C−C str.	1108		
ν_{19}, C−H bend	1117	**ν_{19}, CCC bend**	**1147**	**1175**	
ν_{20}, C−H bend + NH_2 rock	1231	ν_{20}, C−C str. + C−H bend	1256		
ν_{21}, C−C str. + NH_2 rock	1321	ν_{21}, C−C str. + C−H bend + C−N str.	1341		
ν_{22}, C−C str.+C−N str.	1327	**ν_{22}, C−C stretch,NH_2rock**	**1379**	**1370**	
ν_{23}, C−C str. + C−N str.	1374	ν_{23}, C−C str. + NH_2 rock	1413		
ν_{24}, asym. C−C str.	1404	**ν_{24}, NH_2 scissor + C−C stretch +N−C stretch**	**1443**	**1460**	
ν_{25}, NH_2 bend+C−C str. +C−H bend +C−N str.	1514	**ν_{25}, C−C str., NH_2 rock**	**1465**	**1475**	
ν_{26},asym. C−C str.	1604	**ν_{26}, NH_2 scissor, + C−C stretch +N−C stretch**	**1554**	**1498**	
ν_{27}, NH_2 scissor + C−N str.	1611	**ν_{27}, NH_2Scissor+C−N str.**	**1609**	**1534**	
ν_{28},C−H str.	3123	ν_{28}, C−H str.	3128		
		4-Oxocyclohexa-dienylidene			
ν_2, ring def.	257	ν_2, ring def.	340 (299) [−41]		
ν_3, ring def.	390	ν_3, ring def.	426 (494) [−22]		
ν_4, ring def.	442	ν_4, ring def.	467 (395) [72]		
ν_5, ring def.	465	**ν_5, ring def.**	**511 (500) [−11]**	**506**	
ν_6, CCC bend	520	**ν_6, ring def.**	**550 (535) [−15]**	**560**	
ν_7, ring def.	655	ν_7, ring def.	696 (608) [−88]		
ν_8, ring def.	740	**ν_8, C−H bend (o.p.)**	**733 (569) [−164]**	**743**	
ν_9, ring def.	744	**ν_9, C−C stretch**	**766 (690) [−76]**	**768**	
ν_{10}, ring def.	795	**ν_{10}, ring def.**	**814 (695) [−119]**		**819 (706) [−113]**
ν_{11}, ring def.	852	**ν_{11}, C−O str.+C−C str.**	**921 (911) [−10]**		**937 (929) [−8]**
ν_{12}, C−H bend (o.p.)	892	ν_{12}, asym. C−H bend (o.p.)	930 (750) [−180]		
ν_{13}, C−H bend (o.p.)	918	ν_{13}, C−H bend (o.p.)	938 (807) [−131]		
ν_{14}, C−H bend	994	ν_{14}, C−C str.	984 (844) [−140]		
ν_{15}, C−H bend	1057	**ν_{15}, C−H bend**	**1052 (771) [−281]**		**1076**
ν_{16}, C−H bend	1111	**ν_{16}, C−H bend**	**1104 (795) [−309]**	**1123**	
ν_{17}, C−H bend + C−O bend	1193	**ν_{17}, C−H bend + C−C str.**	**1209 (951) [−258]**	**1213**	
ν_{18}, asym. C−C str. + C−H bend	1281	**ν_{18}, C−C str. +C−H bend**	**1288 (1237) [−51]**		**1260**
ν_{19}, C−H bend + C−O str.	1339	**ν_{19}, C−H bend**	**1349 (1208) [-141]**		**1362**
ν_{20}, C−C str.	1362	**ν_{20}, C−H bend + C−C str.**	**1359 (1333) [−26]**		**1375 (1298) [−77]**
ν_{21}, asym. C−C str.	1453	ν_{21}, C−H bend + C−C str.	1464 (1435) [−29]		
ν_{22}, C−C str. + C−O str.	1457	**ν_{22}, C−C str. + C−O str.**	**1485 (1453) [−32]**	**1512**	**1496 (1487) [−9] ?**
ν_{23}, C−C str. + C−O str.	1586	**ν_{23}, C−C str. + C−O str.**	**1496 (1486) [−10]**	**1517**	**1496 (1487) [−9] ?**
ν_{24}, C−H str.	3103	ν_{24}, C−H str.	3112		

[a] str. = stretch; sym. = symmetric; asym. = asymmetric; def. = deformation.

transient resonance Raman spectra shown in Figure 2. Examination of Figure 2 reveals that nine and eight Raman bands are observed for the 4-iminocyclohexa-2,5-dienylidene and 4-oxocyclohexa-2,5-dienylidene carbenes, respectively. Comparison of experimental vibrational frequencies to those predicted by ab initio and density functional theory calculations have proven useful to assign a number of transient species including several carbenes.[26,31,33−37,43−53] In particular, density functional theory methods such as B3LYP and BPW91 have proven computationally cost-effective to predict vibrational frequencies that are in close agreement with those observed in either time-resolved infrared (TRIR) and time-resolved resonance Raman (TR^3) experiments of arylnitrenium ions[37,49,50] and several carbenes.[51,53] Therefore, we have used density functional theory calculations (BPW91/cc-PVDZ for the singlet state and UBPW91/cc-PVDZ for the triplet state) to find the optimized geometry and vibrational frequencies for the singlet and triplet states of 4-iminocyclohexa-2,5-dienylidene and 4-oxocyclohexa-2,5-dienylidene carbenes (selected values are shown in Table 1 for vibrational frequencies and Table 2 for geometry parameters). Figure 3 depicts simple diagrams of the 4-iminocyclohexa-2,5-dienylidene and 4-oxocyclohexa-2,5-dienylidene carbenes with their atoms numbered as given in Table 2. The Supporting Information provides Cartesian coordinates and total energies

TABLE 2: Selected Optimized Geometry Parameters from (U)BPW91/cc-PVDZ Computations for the Triplet (U) and Singlet States of 4-Iminocyclohexa-dienylidene and 4-Oxocyclohexa-2,5-dienylidene Carbene Species[a]

structural parameter	singlet BPW91/cc-PVDZ	triplet UBPW91/cc-PVDZ
4-Iminocyclohexa-dienylidene		
C1−C2	1.4364	1.4455
C2−C3	1.4087	1.3878
C3−C4	1.3663	1.4032
C4−C5	1.3663	1.4032
C5−C6	1.4087	1.3878
C6−C1	1.4364	1.4455
C1−N7	1.3523	1.3441
C2−H, C6−H	1.0998	1.0994
C3−H, C5−H	1.0997	1.0987
N7−H12, N7−H14	1.0202	1.0239
C1−C2−C3	120.7	119.4
C2−C3−C4	108.8	116.7
C3−C4−C5	133.8	126.8
C4−C5−C6	108.8	116.7
C5−C6−C1	120.7	119.4
C6−C1−C2	119.8	120.9
C1−N7−H	121.3	121.5
C1−C2−H8	120.9	119.7
C2−C3−H9	123.1	121.4
C4−C5−H10	127.0	121.9
C5−C6−H11	118.3	120.9
4-Oxocyclohexa-dienylidene		
C1−C2	1.4015	1.4003
C2−C3	1.3909	1.3914
C3−C4	1.4749	1.4672
C4−C5	1.4747	1.4672
C5−C6	1.3904	1.3914
C6−C1	1.4019	1.4003
C4−O7	1.2505	1.2608
C2−H, C6−H	1.1001	1.0996
C3−H, C5−H	1.1003	1.0995
C1−C2−C3	113.5	116.8
C2−C3−C4	121.2	121.3
C3−C4−C5	116.4	117.3
C4−C5−C6	121.1	121.3
C5−C6−C1	113.7	116.8
C6−C1−C2	124.2	126.6
C1−C2−H8	122.6	121.7
C2−C3−H9	121.5	121.9
C3−C4−O7	121.7	121.3
C4−C5−H10	117.1	116.9
C5−C6−H11	122.1	121.5

[a] Bond lengths are in Å, and bond angles are in degrees. The atom numbering follows that shown in Figure 3.

computed from the density functional theory calculations of the singlet and triplet states of 4-iminocyclohexa-2,5-dienylidene and 4-oxocyclohexa-2,5-dienylidene carbenes.

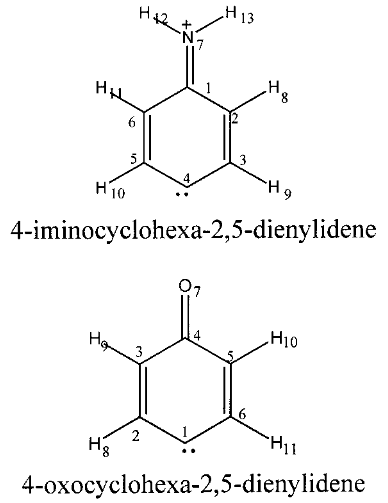

Figure 3. Schematic diagrams of 4-iminocyclohexa-dienylidene (top) and 4-oxocyclohexa-2,5-dienylidene (bottom) carbene species. The numbering of the atoms corresponds to those shown in Table 2.

The vibrational frequencies of the eight resonance Raman bands observed for the 4-oxocyclohexa-2,5-dienylidene carbene in Figure 2 display reasonable agreement with those computed from either of the UBPW91 calculations for the triplet state. For example, the computed UBPW91 values for the triplet state are within about 12 cm^{-1} on average with the experimental Raman values. This is similar to the level of agreement between BPW91/cc-PVDZ computed vibrational frequencies and the transient resonance Raman experimental vibrational frequencies found previously for the singlet 2-fluorenylnitrenium ion (with differences usually between 2 and 8 cm^{-1}).[37] There is substantially worse agreement between the BPW91/cc-PVDZ computed vibrational frequencies for the singlet 4-oxocyclohexa-2,5-dienylidene carbene and the transient resonance Raman band frequencies in Table 1. For example, the experimental Raman bands at 506 and 560 cm^{-1} are significantly farther from the nearest computed values for the singlet state (ν_5 at 465 cm^{-1} and ν_6 at 520 cm^{-1}) compared to the triplet state (ν_5 at 511 cm^{-1} and ν_6 at 550 cm^{-1}). Similarly, the experimental Raman bands at 1512 and 1517 cm^{-1} are in substantially worse agreement with those predicted for the singlet state (ν_{22} at 1457 cm^{-1} and ν_{23} at 1586 cm^{-1}) compared to those predicted for the triplet state (ν_{22} at 1485 cm^{-1} and ν_{23} at 1496 cm^{-1}). The 4-oxocyclohexa-2,5-dienylidene carbene has been previously studied in low-temperature Ar solvent and characterized using infrared absorption and ultraviolet/visible absorption spectroscopies.[26,31] Comparison of the low temperature infrared vibrational frequencies for the 4-oxocyclohexa-2,5-dienylidene carbene with those computed from the UBPW91/cc-PVDZ calculations shows that the infrared bands can be reasonably assigned to the predicted vibrational frequencies. The moderate differences between the Raman and infrared band vibrational frequencies for the ν_{23} and ν_{22} vibrational modes is most likely due to the different solvent (water versus Ar) and phases (room temperature liquid versus low temperature 10 K solid) between the two experiments. We also computed the vibrational frequencies for the fully deuterated triplet 4-oxocyclohexa-2,5-dienylidene carbene and compared the computed frequency shift to the experimental infrared frequency shifts. There is excellent agreement between the infrared experiment and predicted fully deuterated isotopic shifts observed for the ν_{10}, ν_{11}, and ν_{23} vibrational modes. The agreement is not as good for the ν_{20} mode, and this may be due to some mixing between the ν_{20} and ν_{19} modes that are within 13 cm^{-1} of each other. Most of the observed experimental Raman and infrared vibrational frequencies are complementary to one another except for the ν_{22} and/or ν_{23} vibrational modes that are relatively strong in both the Raman and infrared spectra of the 4-oxocyclohexa-2,5-dienylidene carbene. Our results are consistent with previously reported infrared spectra[31] and confirm the assignment of the 4-oxocyclohexa-2,5-dienylidene carbene to a ground triplet state in room-temperature aqueous solutions.[24]

The vibrational frequencies of the nine resonance Raman vibrational frequencies observed for the 4-iminocyclohexa-2,5-dienylidene carbene in Figure 2 exhibit reasonable agreement with the calculated vibrational frequencies for the triplet state. Most of the vibrational frequencies are within about 25 cm^{-1} on average with the experimental Raman values. There is substantially worse agreement between the BPW91/cc-PVDZ computed vibrational frequencies for the singlet 4-iminocyclo-

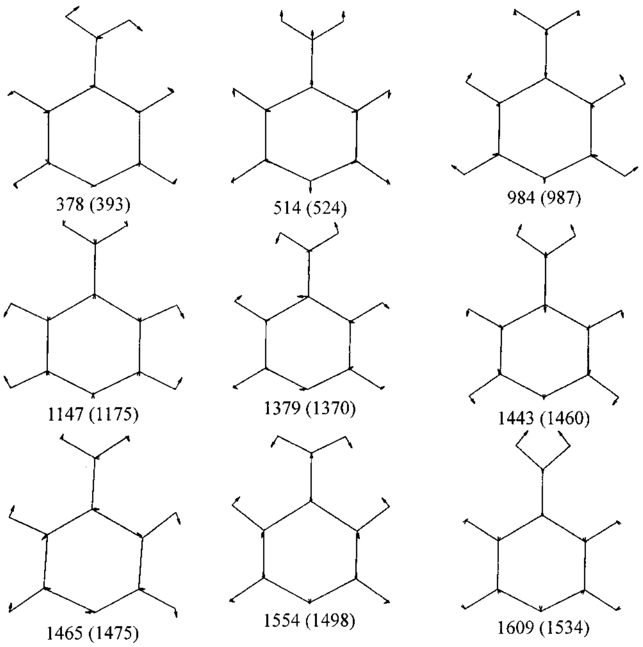

Figure 4. Diagrams shown for the nine vibrational modes observed for the 4-iminocyclohexa-dienylidene carbene in Figure 2. The normal mode vibrational motions are shown in terms of internal coordinate changes by arrows as determined from the BPW91/cc-PVDZ computations. Each diagram is labeled with the DFT computed vibrational frequency (in cm^{-1}), and the Raman experimental value is shown in parentheses.

hexa-2,5-dienylidene carbene and the transient Raman band frequencies shown in Table 1. For example, the 1175 cm^{-1} Raman band is noticeably further away from the singlet computed bands of 1117 and 1231 cm^{-1} compared to the triplet band computed to be at 1147 cm^{-1}. There are two Raman bands at 1460 and 1475 cm^{-1} that display good agreement with the computed triplet bands at 1443 and 1465 cm^{-1}, respectively, but poor agreement with the nearest computed singlet bands at 1404 and 1514 cm^{-1}. The computed frequencies for the singlet ν_{26} and ν_{27} modes are close together (at 1604 and 1611 cm^{-1} with a difference of only 7 cm^{-1}), whereas those for the triplet state are further apart (at 1554 and 1609 cm^{-1} with a difference of about 55 cm^{-1}). The computed triplet ν_{26} and ν_{27} modes are more similar than the computed singlet bands to the observed Raman bands at 1498 and 1534 cm^{-1} (with a difference of about 36 cm^{-1}). The transient resonance Raman band frequencies and comparison to the computed vibrational frequencies of the singlet and triplet states of 4-iminocyclohexa-2,5-dienylidene carbene are consistent with and confirm the proposed assignment of the transient absorption with maxima at 390 and 407 nm in aqueous solutions being due to a 4-iminocyclohexa-2,5-dienylidene carbene in a triplet ground state.[32]

The transient resonance Raman spectrum of the 4-iminocyclohexa-2,5-dienylidene carbene shown in Figure 2 has most of its Raman intensity associated with vibrational modes associated with the NH_2^+ moiety and C−N bond as well as some intensity in C−C stretch and CCC bend modes. The transient resonance Raman spectrum of the 4-oxocyclohexa-2,5-dienylidene carbene shown in Figure 2 has most of its Raman intensity in vibrational modes associated with the C−O bond and C−C stretch motions and some intensity in modes with ring deformation and C−H bend motions. Figures 4 and 5 present simple schematic diagrams of the normal mode descriptions for the nine vibrational modes observed for the triplet 4-iminocyclohexa-2,5-dienylidene carbene and the eight vibrational modes observed for the triplet 4-oxocyclohexa-2,5-dienylidene carbene in the transient resonance Raman spectra shown in Figure 2. The experimental Raman vibrational frequencies are shown in parentheses in Figures 4 and 5. Examination of Figures 4 and 5 reveals that the normal mode descriptions are somewhat complex and are composed of contributions from a number of internal coordinate motions. Therefore, it is useful to use the predicted geometry obtained from the density functional theory calculations to help assess how much the Raman vibrational frequencies correlate with the structure and bond order of the two carbenes. Selected optimized geometry parameters from the density functional theory computations are listed in Table 2 for the singlet and triplet states of the 4-iminocyclohexa-2,5-dienylidene and 4-oxocyclohexa-2,5-dienylidene carbenes.

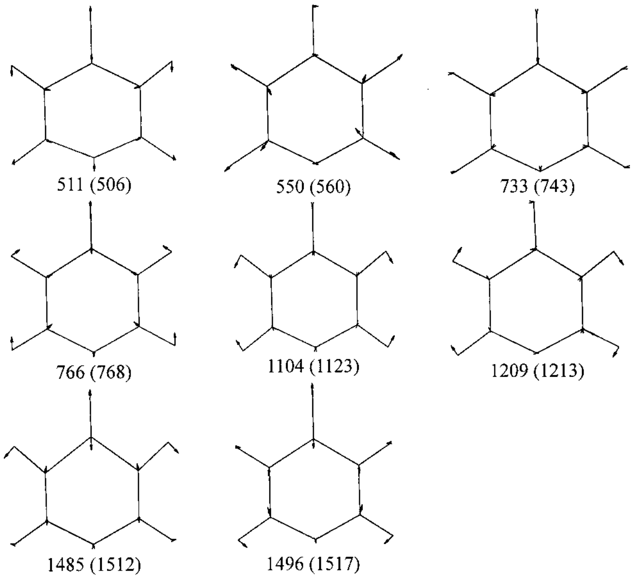

Figure 5. Diagrams shown for the eight vibrational modes observed for the 4-oxocyclohexa-2,5-dienylidene carbene in Figure 2. The normal mode vibrational motions are shown in terms of internal coordinate changes by arrows as determined from the BPW91/cc-PVDZ computations. Each diagram is labeled with the DFT computed vibrational frequency (in cm^{-1}), and the Raman experimental value is shown in parentheses.

Inspection of Table 2 reveals that the carbon−nitrogen bond in the triplet 4-iminocyclohexa-2,5-dienylidene carbene has a bond length of about 1.344 Å which is somewhat close to a partial carbon−nitrogen bond length found in heterocyclic systems such as C_5H_5N (where the C−N bond length is 1.352 Å)[54] compared to a typical carbon−nitrogen double bond (~1.28 Å)[55] or carbon−nitrogen single bond (~1.40 Å).[55] The bond order of the C−N bond in the triplet 4-iminocyclohexa-2,5-dienylidene carbene appears to be close to about 1.5. However, the C=O bond length of 1.2608 Å found in the triplet 4-oxocyclohexa-2,5-dienylidene carbene is close to that found for a carbon−oxygen bond length in ketones (1.23 Å)[54] or in zwitterion systems such as DL serine (1.26 Å).[54] This indicates the carbon−oxygen bond in the 4-oxocyclohexa-2,5-dienylidene carbene has a bond order close to 2 and appears to have some zwitterionic character. It is interesting that the carbon−carbon bonds near the carbene site in both triplet carbenes have very similar bond lengths (1.4003 Å for C1−C2 and C1−C6 in the triplet 4-oxocyclohexa-2,5-dienylidene compared to 1.4032 Å for C4−C5 and C4−C3 in the triplet 4-iminocyclohexa-2,5-dienylidene). There are more noticeable differences between the carbon−carbon bond lengths near the $-NH_2^+$ and C=O moieties of the triplet 4-iminocyclohexa-2,5-dienylidene and

TABLE 3: Spin Density Distributions for the Triplet 4-Iminocyclohexa-2,5-dienylidene and 4-Oxocyclohexa-2,5-dienylidene Carbenes Computed Using UBPW91/cc-PVDZ Computations

triplet 4-iminocyclohexa-2,5-dienylidene		triplet 4-oxocyclohexa-2,5-dienylidene	
parameter	calc. spin density	parameter	calc. spin density
ρ_{C4}	1.31	ρ_{C1}	1.30
ρ_{C5}, ρ_{C3}	−0.09	ρ_{C2}, ρ_{C6}	−0.14
ρ_{C6},ρ_{C2}	0.21	ρ_{C3},ρ_{C5}	0.31
ρ_{C1}	0.10	ρ_{C4}	−0.05
ρ_{N}	0.34	ρ_{O}	0.38
ρ_{H10}, ρ_{H9}	0.02	ρ_{H8}, ρ_{H11}	0.02
ρ_{H11}, ρ_{H8}	0.001	ρ_{H9}, ρ_{H10}	−0.001
ρ_{H12}, ρ_{H13}	−0.01		

4-oxocyclohexa-2,5-dienylidene carbenes. For example, the C6−C1 and C1−C2 bond lengths are about 1.4455 Å for triplet 4-iminocyclohexa-2,5-dienylidene compared to C3−C4 and C4−C5 bond lengths of about 1.4672 Å for triplet 4-oxocyclohexa-2,5-dienylidene. The middle carbon−carbon bonds of the phenyl ring are moderately different in the two triplet carbenes (C6−C5 and C2−C3 have bond lengths of ∼1.3878 Å for 4-iminocyclohexa-2,5-dienylidene compared to 1.3914 Å for 4-oxocyclohexa-2,5-dienylidene). The C1−C6, C1−C2, C6−C5, and C2−C3 carbon−carbon bonds of 4-iminocyclohexa-2,5-dienylidene are shorter and have a moderately higher bond order than the corresponding C4−C3, C4−C5, C5−C6, and C3−C2 carbon−carbon bonds of 4-oxocyclohexa-2,5-dienylidene. The cyclohexadienyl character of these bonds is somewhat larger for 4-oxocyclohexa-2,5-dienylidene (a carbon−carbon bond alternation of about 0.0848 Å) compared to 4-iminocyclohexa-2,5-dienylidene (a carbon−carbon bond alternation of about 0.0577 Å). The higher bond order of the C═O bond and the greater cyclohexadienyl character of the triplet 4-oxocyclohexa-2,5-dienylidene suggests that the C═O moiety interacts with the phenyl ring and carbene more effectively than the $-NH_2^+$ moiety does in the triplet 4-iminocyclohexa-2,5-dienylidene system.

It is interesting to compare the computed spin densities for the triplet 4-iminocyclohexa-2,5-dienylidene and 4-oxocyclohexa-2,5-dienylidene carbenes. Table 3 presents the calculated spin densities of the carbon, nitrogen (or oxygen), and hydrogen atoms determined using a Mulliken population analysis of the UBPW91/cc-PVDZ results. We note the caveat that Mulliken population analyses provide atomic charge spin densities that can noticeably depend on the particular basis set and computational methods employed.[56] Thus, the spin densities shown in Table 3 should be used with some caution. However, the qualitative behavior of the spin densities is interesting to examine. The spin density on the carbon atom associated with the carbene is almost the same in both species (about 1.30−1.31), and this is consistent with the very small geometry differences observed for the carbon−carbon bonds in this region. The spin density on the nitrogen (about 0.34) is similar to that located on the oxygen atom (about 0.38). However, the interaction of the NH_2^+ and oxygen moieties with the phenyl ring appears to lead to some noticeable differences in the spin densities. For example, the oxygen appears to lead to a polar C═O bond with a noticeable negative charge on the carbon atom and a greater spin density alternation on the noncarbene carbon atoms (ρ_{C3},ρ_{C5} = 0.31 and ρ_{C2}, ρ_{C6} = −0.14). However, the $-NH_2^+$ group donates some charge to the corresponding carbon atom to give it a positive charge (ρ_{C1} = 0.10) and a smaller spin density alternation on the noncarbene carbon atoms (ρ_{C6},ρ_{C2} = 0.21 and ρ_{C5}, ρ_{C3} = −0.09). This is consistent with the greater cyclohexadienyl character found for the triplet 4-oxocyclohexa-2,5-dienylidene carbene and its computed carbon−oxygen bond length of 1.2608 Å being close to that of 1.26 Å for typical zwitterionic systems such as DL serine.[54]

Both the triplet 4-iminocyclohexa-2,5-dienylidene and 4-oxocyclohexa-2,5-dienylidene carbenes exhibit very similar chemical reactivity toward oxygen to give iminoquinone and benzoqiunone O-oxide intermediates, respectively.[24,28,29,32] This is consistent with our present results that show that the carbene site and nearest carbon−carbon bonds are almost the same in both species. Grabner and co-workers[24] previously noted that the p_z orbital of the carbene atom could be thought of as the frontier orbital for most reactions, and addition of oxygen (O_2) gives rise to the iminoquinone and benzoqiunone O-oxide intermediates observed in the transient absorption experiments.

Our present results indicate that the triplet 4-iminocyclohexa-2,5-dienylidene and 4-oxocyclohexa-2,5-dienylidene carbenes display noticeably different degrees of cyclohexadienyl character as well as different bond orders for the carbon−nitrogen and carbon−oxygen bonds. These differences should influence the stability of the carbenes in aqueous solution and the chemical reactivity at the −C═O and $-NH_2^+$ groups. A large difference in the photochemistry of 4-chlorophenol and 4-chloroaniline is that the formation of the relevant carbene species only takes place in protic solvents such as water but not in polar nonprotic solvents such as acetonitrile in the case of 4-chlorophenol, whereas the carbene species can be formed in both protic and nonprotic polar solvents in the case of 4-chloroaniline.[24,32] This behavior was rationalized by Grabner and co-workers[32] by a two step process for formation of the carbene via a dehalogenation step followed by a deprotonation step. For the case of a 4-chlorophenol precursor, the deprotonation step is not accessible in nonprotic polar solvents such as acetonitrile, and the 4-oxocyclohexa-2,5-dienylidene carbene species is not formed in these solvents.[24] On the other hand, for 4-chloroaniline, the initially formed carbocation (from the dehalogenation step) and the protonated carbene are tautomeric and the deprotonation step is not needed because the nitrogen atom can accommodate a positive charge, and thus, the 4-iminocyclohexa-2,5-dienylidene carbene species can be generated in both protic and nonprotic polar solvents.[32] The ability of the nitrogen atom to accommodate a positive charge also leads to similar photochemistry for the 4-chloro-*N*,*N*-dimethylanailine in both protic and nonprotic polar solvents,[32] whereas similar derivatives of 4-chlorophenol and 4-chloroanisole do not form the carbene species in nonprotic polar solvents.[24] The chemical reactivity of the $-NH_2^+$ group of the carbene enables the iminoquinone oxide (formed from reaction of O_2 with the 4-iminocyclohexa-2,5-dienylidene carbene) to react with 4-chlorophenol, and this appears to lead to a different product distribution than that found from the reaction of the 4-oxocyclohexa-2,5-dienylidene carbene with O_2.[32]

It is interesting to compare the structure and properties of the 4-iminocyclohexa-2,5-dienylidene carbene with those of arylnitrenium ions in order to better understand the interaction of the $-NH_2^+$ moiety with the phenyl ring versus the interaction of the $-NH^+$ group with the phenyl ring. A number of arylnitrenium ions have singlet ground states,[37,49,50,57] and the C−N bond length (from BPW91/cc-PVDZ computations) ranged from 1.317 to 1.323 Å for four *N*-methyl-N-phenylnitrenium ions[50] and about 1.3077 Å for the 2-fluorenylnitrenium ion.[37] The C−N bond lengths in the 4-iminocyclohexa-2,5-dienylidene carbenes from similar calculations were noticeably longer with values of about 1.3441 Å for the triplet state and

1.3523 Å for the singlet state (note both the singlet and triplet state C−N bond lengths are similar to one another). These values are much more similar to the ∼1.351 Å C−N bond length found for the diphenylnitrenium ion.[49,57,58] The significantly weaker C−N bond in the diphenylnitrenium ion was attributed the charge delocalization being spread over two phenyl rings attached to the NH^+ moiety instead of one phenyl ring in the other arylnitrenium ions.[49,57,58] Our results suggest that changing from an $-NH^+$ group attached a phenyl ring to a $-NH_2^+$ group attached to a phenyl ring is similar to adding a phenyl group to the $-NH^+$ moiety (in other words the added H delocalizes the charge to a similar degree as an additional phenyl ring).

The degree of cyclohexadienyl character of the phenyl ring in the triplet 4-iminocyclohexa-2,5-dienylidene carbene is also noticeably weaker than that found in several arylnitrenium ions. For example, the triplet 4-iminocyclohexa-2,5-dienylidene has a carbon−carbon bond alternation of about 0.0577 Å for the C6−C1 and C1−C2 bond lengths, whereas the bond alternation is about 0.1031 Å for the corresponding bonds in the 2-fluorenylnitrenium ion[37] or about 0.078−0.089 Å in four *N*-methyl-*N*-phenylnitrenium ions.[50] However, the cyclohexadienyl character of the triplet 4-iminocyclohexa-2,5-dienylidene carbene (with a carbon−carbon bond alternation of about 0.0577 Å for the C6−C1 and C1−C2 bond lengths) is very similar to that found for the diphenylnitrenium ion where the bond alternation is about 0.0562 Å for the corresponding bonds.[57] Both the degree of imine character and cyclohexadienyl character suggest that the addition of a hydrogen atom to a $-NH^+$ group attached to a phenyl ring is very similar to addition of a phenyl ring. This indicates the delocalization of charge from the nitrogen atom in an arylnitrenium ion by a second hydrogen atom or a second phenyl ring attached to the nitrogen atom is very similar to one another. Thus, the weaker C−N bond order and cyclohexadienyl character found for the triplet 4-iminocyclohexa-2,5-dienylidene carbene compared to the C−O bond order and cyclohexadienyl character of the triplet 4-oxocyclohexa-2,5-dienylidene carbene appears to be mainly due to the charge delocalization ability of the second hydrogen atom in the $-NH_2^+$ moiety.

It is interesting that the density functional theory calculations appear to predict the vibrational frequencies of arylnitrenium ions somewhat better than for the triplet 4-iminocyclohexa-2,5-dienylidene carbene (especially for the higher frequency modes in the 1500−1700 cm^{-1} region associated with the aromatic ring and nitrogen groups). This is particularly noticeable for the ν_{26} (NH_2 scissor + C−C stretch +N−C stretch) and the ν_{27}, (NH_2 scissor + C−N str.) modes of the triplet 4-iminocyclohexa-2,5-dienylidene carbene that are computed to be at 1554 and 1609 cm^{-1} compared to the observed Raman bands at 1498 and 1534 cm^{-1}, respectively. Semiempirical calculations previously reported for the triplet 4-oxocyclohexa-2,5-dienylidene carbene[24] indicated the possible presence of a noticeable specific carbene−H_2O interaction. It is conceivable that a similar interaction could be noticeably larger in the case of the triplet 4-iminocyclohexa-2,5-dienylidene carbene. There is also the possibility of a greater H_2O interaction with the $-NH_2^+$ group than a $-NH^+$ group (perhaps hydrogen bonding at two H sites versus one H site) and this could also account for the greater differences between the predicted and observed vibrational frequencies for the ν_{26} and ν_{27} modes of the triplet 4-iminocyclohexa-2,5-dienylidene carbene. Because the triplet 4-iminocyclohexa-2,5-dienylidene carbene can be formed in both protic and nonprotic solvents, we plan to explore solvent effects on the structure and properties of this novel carbene.

Conclusions

We have obtained transient resonance Raman spectra of the 4-iminocyclohexa-dienylidene and 4-oxocyclohexa-2,5-dienylidene carbene species in aqueous solutions. Comparison of the Raman vibrational frequencies to those predicted from density functional theory calculations indicates that both carbenes are in their ground triplet states. The 4-oxocyclohexa-2,5-dienylidene carbene has greater cyclohexadienyl character than the 4-iminocyclohexa-dienylidene carbene. The bond order is about 2 for the C=O bond in the 4-oxocyclohexa-2,5-dienylidene carbene compared to a bond order of about 1.5 for the C−N bond in the 4-iminocyclohexa-2,5-dienylidene carbene. Comparison of our results for the 4-iminocyclohexa-dienylidene carbene to those previously found for several arylnitrenium ions found that the imine and cyclohexadienyl character of the 4-iminocyclohexa-dienylidene carbene is very close to that observed for the diphenylnitrenium ion. This indicates that the delocalization of charge from the nitrogen atom in an arylnitrenium ion by a second hydrogen atom or a second phenyl ring attached to the nitrogen atom is very similar to one another. Therefore, the smaller C−N bond order and lower cyclohexadienyl character observed for the triplet 4-iminocyclohexa-2,5-dienylidene carbene compared to the higher C=O bond order and greater cyclohexadienyl character of the triplet 4-oxocyclohexa-2,5-dienylidene carbene is mostly due to the charge delocalization ability of the second hydrogen atom in the $-NH_2^+$ moiety. We briefly discuss the structures and properties of the 4-iminocyclohexa-dienylidene and 4-oxocyclohexa-dienylidene carbenes and how this appears to influence their chemical reactivity.

Acknowledgment. D.L.P. would like to thank the Committee on Research and Conference Grants (CRCG) and the Research Grants Council of Hong Kong (HKU 7214/99P and HKU 7087/01P) for support of this research.

Supporting Information Available: Cartesian coordinates and total energies computed from the density functional theory calculations of the singlet and triplet states of 4-iminocyclohexa-2,5-dienylidene and 4-oxocyclohexa-2,5-dienylidene carbenes. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Grimshaw, J.; De Silva, A. P. *Chem. Soc. Rev.* **1981**, *10*, 181.
(2) Davidson, R. S.; Goodin, I. W.; Kemp, G. *Adv. Phys. Org. Chem.* **1984**, *20*, 191.
(3) Cornelisse, J.; Havinga, E. *Chem. Rev.* **1975**, *75*, 353.
(4) Den Heijer, J.; Shadid, O. B.; Cornelisse, J.; Havinga, E. *Tetrahedron* **1977**, *33*, 779.
(5) Cornelisse, J.; Lodder, G.; Havinga, E. *Rev. Chem. Intermed.* **1979**, *2*, 232.
(6) Miller, G. C.; Mille, M. J.; Crosby, D. G.; Sontum, S.; Zepp, R. G. *Tetrahedron* **1979**, *35*, 1979.
(7) Siegman, J. R.; Houser, J. J. *J. Org. Chem.* **1982**, *47*, 2773.
(8) Avila, V.; Gsponer, H. E.; Previtali, C. *J. Photochem.* **1984**, *27*, 163.
(9) Kropp, P. J. *Acc. Chem. Res.* **1984**, *17*, 131.
(10) Ruzo, L. O.; Sundstrom, G.; Hutzinger, O.; Safe, S. *J. Agric. Food Chem.* **1976**, *24*, 1062.
(11) Totter, W. J. *Bull. Environ. Contam. Toxicol.* **1977**, *18*, 726.
(12) Robertson, L. W.; Parkinson, A.; Safe, S. *Biochem. Biophys. Res. Commun.* **1980**, *92*, 175.
(13) Parkinson, A.; Safe, S. *Toxicol. Environ. Chem. Rev.* **1981**, *4*, 1.
(14) Robertson, L. W.; Parkinson, A.; Campell, M. A.; Safe, S. *Chem. Biol. Interact.* **1982**, *42*, 53.
(15) Miller, F. D.; Brilliant, L. B.; Copeland, R. *Bull. Environ. Contam. Toxicol.* **1984**, *32*, 125.
(16) Boule, P.; Guyon, C. *Toxicol. Environ. Chem.* **1984**, *7*, 97.

(17) Boule, P.; Guyon, C.; Tissot, A.; Lemaire, J. *ACS Symp. Ser.* **1987**, *327*, 10.

(18) Lipcynska-Kochany, E.; Bolton, J. R. *J. Photochem. Photobiol. A: Chem.* **1991**, *58*, 315.

(19) Lipcynska-Kochany, E. *Chemosphere* **1992**, *24*, 911.

(20) Lipcynska-Kochany, E.; Kochany, J. *J. Photochem. Photobiol;. A: Chem.* **1993**, *73*, 23.

(21) Miller, G. C.; Crosby, D. G. *Chemosphere* **1983**, *12*, 1217.

(22) Kaiser, K. L. E.; Palabrica, V. S. *Water Pollut. Res. J. Can.* **1991**, *26*, 361.

(23) Coquart, V.; Hennion, M.-C. *Chromatographia* **1993**, *37*, 392.

(24) Grabner, G.; Richard, C.; Köhler, G. *J. Am. Chem. Soc.* **1994**, *116*, 11470.

(25) Sander, W.; Müller, W.; Sustmann, R. *Angew. Chem.* **1988**, *100*, 577.

(26) Sander, W.; Bucher, G.; Reichel, F.; Cremer, D. *J. Am. Chem. Soc.* **1991**, *113*, 5311.

(27) Bucher, G.; Sander, W. *J. Org. Chem.* **1992**, *57*, 1346.

(28) Arnold, B. R.; Sciano, J. C.; Bucher, G. F.; Sander, W. *J. Org. Chem.* **1992**, *57*, 6469.

(29) Sander, W. *J. Org. Chem.* **1988**, *53*, 2091.

(30) Wasserman, E.; Murray, R. W. *J. Am. Chem. Soc.* **1964**, *86*, 4203.

(31) Sander, W.; Müller, W.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 572.

(32) Othmen, K.; Boule, P.; Szczepanik, B.; Rotkiewicz, K.; Grabner, G. *J. Phys. Chem. A* **2000**, *104*, 9525.

(33) Pan, D.; Shoute, L. C. T.; Phillips, D. L. *J. Phys. Chem. A* **2000**, *104*, 4140.

(34) Zheng, X.; Phillips, D. L. *J. Phys. Chem. A* **2000**, *104*, 6880.

(35) Zheng, X.; Kwok, W. M.; Phillips, D. L. *J. Phys. Chem. A* **2000**, *104*, 10464.

(36) Zheng, X.; Lee, C. W.; Li, Y.-L.; Fang, W.-H.; Phillips, D. L. *J. Chem. Phys.* **2001**, *114*, 8347.

(37) Zhu, P.; Ong, S. Y.; Chan, P. Y.; Leung, K. H.; Phillips, D. L. *J. Am. Chem. Soc.* **2001**, *123*, 2645.

(38) Li, Y.-L.; Leung, K. H.; Phillips, D. L. *J. Phys. Chem. A* **2001**, *105*, 10621.

(39) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(40) Becke, A. *J. Chem. Phys.* **1986**, *84*, 4524.

(41) Perdew, J. P.; Burke, K.; Wang, Y. *Phys. Rev. B* **1996**, *54*, 16533.

(42) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(43) Buntinx, G.; Poizat, O. *J. Chem. Phys.* **1989**, *91*, 2153.

(44) Sasaki, Y.; Hamaguchi, H. *Spectrochim. Acta* **1994**, *50A*, 1475.

(45) Furuya, K.; Torii, H.; Furukawa; Tasumi, M. *Chem. Lett.* **1996**, 913.

(46) Keszthelyi, T.; Wilbrandt, R.; Bally, T. *J. Phys. Chem.* **1996**, *100*, 16843.

(47) Keszthelyi, T.; Wilbrandt, R.; Bally, T.; Roulin, J. L. *J. Phys. Chem.* **1996**, *100*, 16850.

(48) Mohandas, P.; Umapathy, S. *J. Phys. Chem. A* **1997**, *101*, 4449.

(49) Srivastava, S.; Toscano, J. P.; Moran, R. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1997**, *119*, 11552.

(50) Srivastava, S.; Ruane, P. H.; Toscano, J. P.; Sullivan, M. B.; Cramer, C. J.; Chiapperino, D.; Reed, E. C.; Falvey, D. E. *J. Am. Chem. Soc.* **2000**, *122*, 8271.

(51) Sander, W.; Hübert, R.; Kraka, E.; Gräfenstein, J.; Cremer, D. *Chem. Eur. J.* **2000**, *6*, 4567.

(52) Puranik, M.; Chandrasekhar, J.; Snijders, J. G.; Umapathy, S. *J. Phys. Chem. A* **2001**, *105*, 10562.

(53) Tsao, M.-L.; Zhu, Z.; Platz, M. S. *J. Phys. Chem. A* **2001**, *105*, 8413.

(54) *CRC Handbook of Chemistry and Physics*, 62nd ed.; CRC Press: Boca Raton, FL, 1982.

(55) March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977.

(56) Mulliken, R. S.; Ermler, W. C. *Diatomic Molecules*; Academic: New York, 1977.

(57) Zhu, P.; Ong, S. Y.; Chan, P. Y.; Poon, Y. F.; Leung, K. H.; Phillips, D. L. *Chem. Eur. J.* **2001**, *7*, 4928.

(58) Cramer, C. J.; Falvey, D. E. *Tetrahedron Lett.* **1997**, *38*, 1515.