

Excited States of the Allene Chromophore: Photoelectron, Circular Dichroism, and Absorption Spectroscopy of Alkyl- and Halogenoallenes¹

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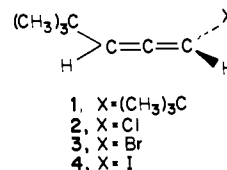
Contribution from the Department of Organic Chemistry, State University, Utrecht, The Netherlands, the Department of Chemistry, Bar-Ilan University, Ramat-Gan 52100, Israel, and the Institut für Struktur- und Systemforschung, D-6900 Heidelberg, West Germany. Received January 10, 1984

Abstract: Photoelectron (PE) as well as near- and vacuum-ultraviolet (300–150 nm) absorption and circular dichroism (CD) spectra of the *tert*-butylallenes (CH₃)₃CCH=C=CHX (X = C(CH₃)₃, Cl, Br, I) are reported. The emphasis of the work is on the excited states and electronic structures of the allenes. In the PE spectra interactions between the substituents across the allenic C=C=C system are observed. These can be rationalized in terms of Coulombic field effects and “hyperconjugation”. Effects of vibronic coupling observed in the PE spectra are discussed qualitatively. By the combined use of absorption and CD spectroscopy, a large number of excited states resulting from valence-shell and Rydberg transitions are observed. The assignments of Rydberg states rely essentially on the absorption spectra using ionization energies from the PE spectra. Referring to the hydrocarbon as a representative of the allene chromophore, the sequence of excited states resulting from intravalence e → e (HOMO → LUMO) transitions is found to be ¹A₂ < ¹B₁ < ¹B₂ < ¹A₁. The intravalence excited states of the halogenoallenes originating with the two highest energy orbitals can be correlated with those of the allene chromophore. The two lowest energy excited states of chloro- and iodoallene are shown to have bent C=C=C geometries. In the CD spectra of the halogenoallenes low-energy excited states are detected with the corresponding electronic transitions terminating at the antibonding C-X σ orbitals (σ*_{C-X}) and σ*_{C-X} comprising halogen d atomic orbitals.

I. Introduction

Electronic structures of allenes as prototypes of “nonplanar π-systems” have received considerable attention in the last decade.^{3,4} However, there remain a number of open questions. These generally concern problems of interactions between substituents and the allenic skeleton⁴ as well as interactions between the substituents across the allenic system.^{1,4} Specific problems refer to interactions of heteroatom lone pairs with the allenic “double bonds”⁵ and the involvement of the substituents’ d atomic orbitals (AOs) in the ground and excited states of these molecules.^{1,4-6} In particular, the nature and sequence of excited states of the “allene chromophore” represent a field of continuing confusion.^{3,7} This is true even for the parent molecule allene (H₂C=C=CH₂) (5)⁷⁻⁹ and its simple alkyl derivatives.^{10,11}

The present work intends to contribute to the elucidation of the above problems through the simultaneous investigations of the He I photoelectron (PE) as well as near- (UV) and vacuum-ultraviolet (vacuum-UV) absorption and circular dichroism (CD) spectra of the series of optically active allenes 1–4 (whose absolute



configurations have been determined to be (*R*)-(-) in an accompanying paper¹²). The wavelength region covered is 300–150 nm. The emphasis will be on the excited states of 1–4.

Not only do problems with the assignments of excited states of allenes stem from severe overlap of the electronic bands for the largest parts of the absorption spectra, but also further complications are due to the simultaneous existence of very weak and medium to strong absorption bands that are related to magnetic dipole allowed (MA), electric dipole forbidden (EF) transitions and electric dipole allowed (EA), magnetic dipole forbidden (MF) transitions, respectively.^{3,5a,6,13,14} Especially in absorption studies, the weak electronic bands are buried in the strong ones. Natural circular dichroism of chiral molecules is a key method to overcome the above problem in detecting MA,EF transitions. For allenes the potential of the combined use of UV absorption and CD spectroscopy has been demonstrated for various types of molecules.^{13,14} Similarly, the combination of absorption and CD spectroscopy has provided detailed insights into the excited states of the ethylene chromophore^{15,16} which is structurally related to the allene chromophore.^{3b,4,5a,6,13} In allene (5) (of symmetry *D*_{2d}) the outermost (occupied and unoccupied) molecular orbitals (MOs) 2e and 3e are composed of degenerate π- and π*-type orbitals, respectively.³ Thus, the 2e orbital may be thought of as being composed of two π-type orbitals, say, π_y and π_z. Owing

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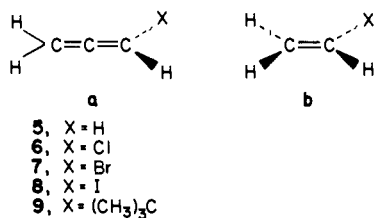
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to the small perturbations induced by alkyl substituents in alkylated allenes, the electronic states of the substituted allenes are similar to those of the parent. In particular, 1,3-dialkylation (associated with a symmetry reduction from D_{2d} to C_2) does not lead to a distinct separation of the allenic e orbitals.³ In 1,3-dialkylallenes the outermost MOs remain accidentally degenerate, and the electronic ground state and excited states of 1,3-dialkylallenes can be correlated and directly compared with those of allene (**5**); i.e., they represent the allenic chromophore. Hence, for 1,3-di-*tert*-butylallene (**1**) the classification of electronic states will be done according to its effective D_{2d} symmetry, and the selection rules for electronic transitions are essentially identical with those of **5**. The excited intravalence singlet states of allene (**5**) that are lowest in energy arise from promoting an electron from the $2e$ to the $3e$ orbital.³ This $2e \rightarrow 3e$ excitation produces four excited (singlet) states, 1A_1 , 1A_2 , 1B_1 , and 1B_2 , involving appropriate linear combinations of the electronic configurations, (π_z, π^*_y) , (π_y, π^*_z) , (π_x, π^*_z) , and (π_y, π^*_y) .³ Experimental assignment of these states and earlier quantum-chemical calculations are in agreement only with respect to the order $^1A_2 < ^1B_1 < ^1B_2$, the position of the 1A_1 state being questionable.³ Also recent ab initio calculations are controversial, for instance, $^1B_2 < ^1A_1$ in ref 7a but $^1A_1 < ^1B_2$ in ref 7b.^{7c}

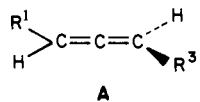
Owing to their conjugative powers and polarities, halogen atoms as substituents generally induce larger perturbations of electronic states than alkyl groups. As a consequence, substitution of one *tert*-butyl group in **1** by halogen atoms (**1** \rightarrow **2-4**) should lift the degeneracy of the outermost e -type orbitals of **1**; leading to more or less separated $\pi_X (\approx \pi_z)$ and $\bar{\pi}_{Alk} (\approx \pi_y)$ orbitals.³ The former comprise the double bond adjacent to the halogen atom ($X = \text{Cl, Br, I}$) and correlate with the $\pi(a'')$ orbitals of the halogenoallenes **6a-8a**, whereas $\bar{\pi}_{Alk}$ orbitals comprise the double bond adjacent



to the alkyl group. The $\bar{\pi}_{Alk}$ orbital correlates with the $\pi(a'')$ orbital in *tert*-butylallene (**9a**).

Due to the relatively small influence of an alkyl group on molecular electronic states the alkylated halogenoallenes **2-4** may be viewed as slightly perturbed halogenoallenes **6a-8a**.^{3b} Assignments of PE and electronic bands, therefore, will advantageously refer to correlations with corresponding bands (states) in **6a-8a**. On this level comparisons with the situations in the structurally related ethylenes (**b**) may be guidelines for band assignments and will provide insight into the electronic structures of the allenes.³⁻⁶

The notations of the outermost orbitals of the halogenoallenes **2-4** according to π_X and $\bar{\pi}_{Alk}$, however, do not mean that they remain "pure"; i.e., π_X and $\bar{\pi}_{Alk}$ do not mix. In general, in 1,3-disubstituted allenes (**A**) the lack of any geometrical symmetry allows a mixture of these orbitals (breakdown of the $\pi-\sigma(\bar{\pi})$ separation).^{3,4} Then, the resulting orbitals should be described according to eq 1a and 1b. In eq 1, N_- and N_+ are normalization



$$\pi_- = N_-(\pi_z - \lambda_- \pi_y) \xrightarrow{R^1 = t\text{-Bu}} \pi_X \quad (1a)$$

$$\pi_+ = N_+(\pi_y + \lambda_+ \pi_z) \xrightarrow{R^3 = X} \bar{\pi}_{Alk} \quad (1b)$$

constants and λ_- and λ_+ mixing coefficients. For molecules with $R^1 = R^3$ and C_2 symmetry, such as **1**, one has $N_- = N_+ = (1/2)^{1/2}$

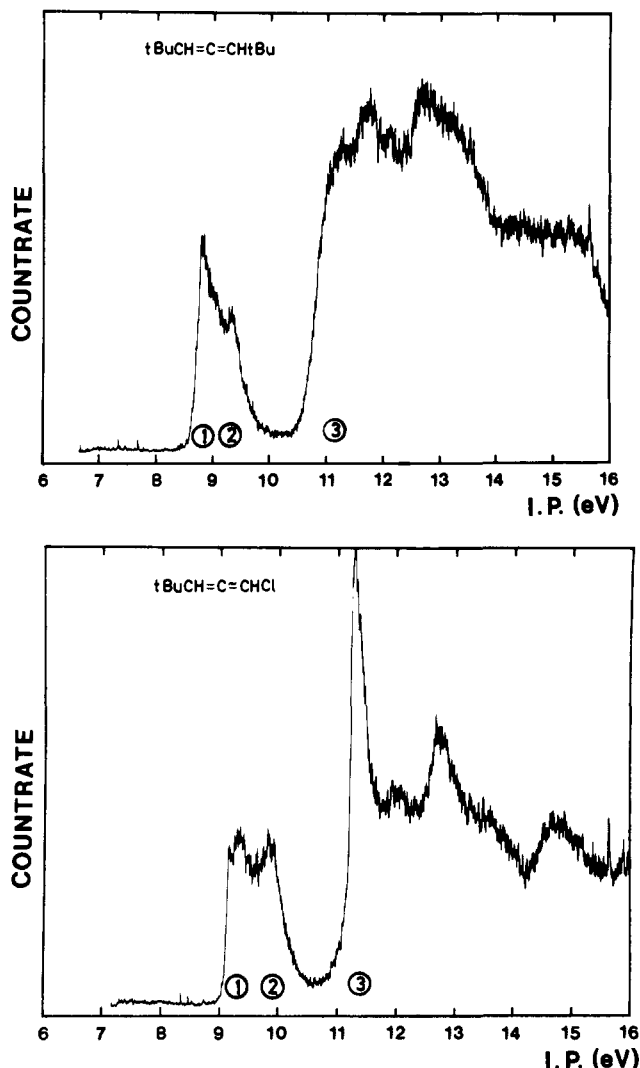


Figure 1. PE spectra of γ -substituted *tert*-butylallenes **1** (top) and **2** (bottom).

and $\lambda_- = \lambda_+ = 1$. The above classification of orbitals of **2-4** according to π_X and $\bar{\pi}_{Alk}$ (or π^*_X and $\bar{\pi}^*_{Alk}$, respectively) then is physically meaningful for $\lambda_- \ll 1$ and $\lambda_+ \ll 1$. Otherwise, the notation π_X and $\bar{\pi}_{Alk}$ refers to the leading term in eq 1a and 1b, respectively.

II. Experimental Section

1. Chemicals. The syntheses of the racemic and optically active allenes **1-4** are described in ref 12. The optical purities of all the compounds studied in this work were ca. 40%. The measured CD data were converted to those of compounds having minimum optical purities of 90%, the corresponding optical rotations then being $[\alpha]_D -124^\circ$ (EtOH) for **1**, $[\alpha]_D -225^\circ$ (EtOH) for **2**, $[\alpha]_D -230^\circ$ (EtOH) for **3**, and $[\alpha]_D -314^\circ$ (EtOH) for **4** (for the purification of **1-4** refer to the accompanying paper¹²).

2. Spectroscopy. The PE spectra were recorded on a Perkin-Elmer PS 18 photoelectron spectrometer. The resolution was ca. 25 meV.

The solution absorption spectra were run with a Perkin-Elmer 555 UV-vis spectrophotometer. The solution CD spectra were measured with a Jouan CD III dichrograph. For both methods spectral resolution at 40000 cm^{-1} was ca. 40 cm^{-1} . Isooctane, *n*-hexane, and CCl_4 (Merck, Uvasol) served as solvents and were used without further purification.

The instrument for the vacuum-UV-CD measurements has been described previously.¹⁸ The modifications introduced into the apparatus were also reported.¹⁵ The monochromator (Mc Pherson 225) was equipped with a 1200-lines/mm grating. The dispersion of this monochromator is $\sim 8 \text{ \AA/mm}$. Absorption and CD measurements were car-

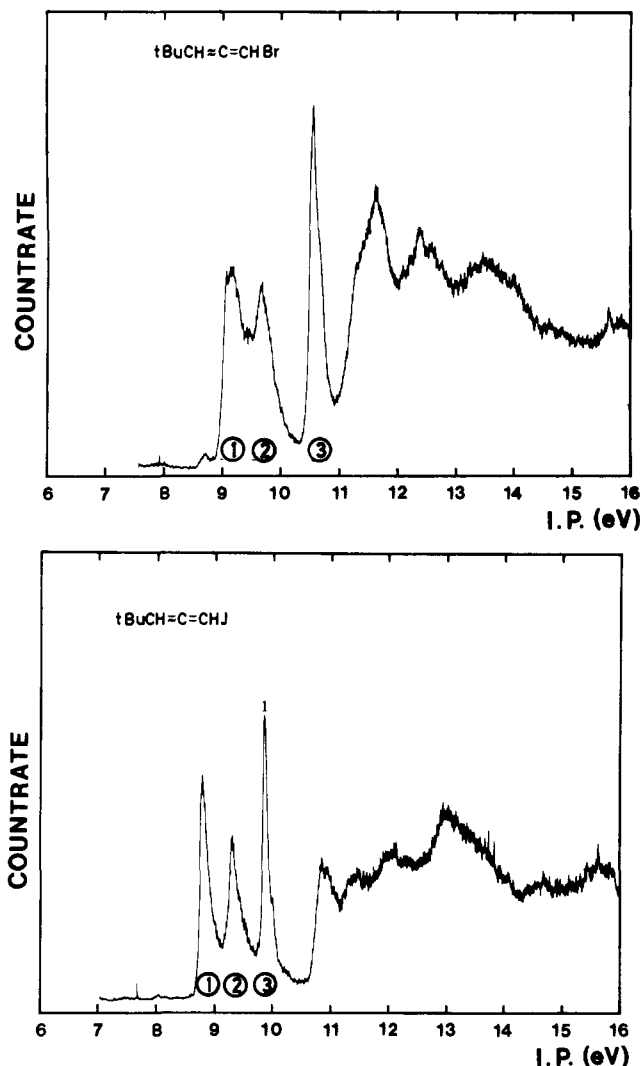


Figure 2. PE spectra of γ -substituted *tert*-butylallenes 3 (top) and 4 (bottom).

ried out with a 2-mm slit width yielding a spectral resolution of ca. 16 Å. Absorption measurements were repeated with a 500- μ m slit width, but no changes were detected. All the measurements were carried out in an 11-cm optical cell. The vapor pressure of the samples was measured by a Clesco P7D capacitance manometer.

III. Results and Discussions

1. PE Spectra. The PE spectra of the allenes 1 and 2 are displayed in Figure 1 and those of 3 and 4 in Figure 2. With regard to the special interest in electronic excited states of the allenes 1-4, the PE bands with energies less than ~ 11 eV are of primary concern in this work. Vertical ionization energies (I_v) and vibrational spacings ($\bar{\nu}^+$) of the three lowest energy PE bands of 1-4 are summarized in Table I. The PE band assignments are, in general, based upon Koopmans' approximation (eq 2),

$$I_v(i) = -\epsilon_i^{\text{SCF}} \quad (2)$$

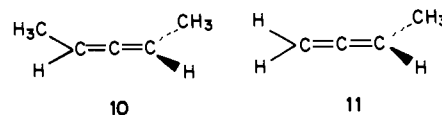
which relates the vertical ionization energy to the negative energy of the MO i (of the neutral molecule) as calculated by an SCF procedure. The approximation loses its validity in several cases which are well-known. For the allenes, in particular, relevant cases refer to ionization from close orbitals or when more than one state originates from the same electronic configuration.^{19,20}

The PE spectrum of 1,3-di-*tert*-butylallene (1) is similar in shape to those of allene (5)^{19,20} and 1,3-dimethylallene (10)^{19a} and exhibits in its low energy part a double humped feature. Bands 1 and 2 of the radical cation 1^+ are characterized by the positions of the fine-structure maxima of highest intensities. The split (Δ

Table I. Vertical Ionization Energies (I_v), Vibrational Spacings ($\bar{\nu}^+$),^a and Assignments of PE Bands of *tert*-Butylallenes ($(\text{CH}_3)_3\text{CH}=\text{C}=\text{CHX}$)

band	I_v , eV	$\bar{\nu}^+$, cm^{-1}	assignment ^b
1 (X = C(CH₃)₃)			
1	8.77	390	e_1
2	9.28	520	e_2
3	11.3	490	$\sigma_{(1)}((\text{CH}_3)_3\text{C}-\text{C})$
2 (X = Cl)			
1	9.30	400	π_{Cl}
2	9.80	650	$\bar{\pi}_{\text{Alk}}$
3	11.25	500	$n_{\text{Cl}}; \sigma_{(1)}((\text{CH}_3)_3\text{C}-\text{C})$
3 (X = Br)			
1	9.10	400 (910)	π_{Br}
2	9.65		$\bar{\pi}_{\text{Alk}}$
3	10.53		n_{Br}
4 (X = I)			
1	8.78		π_{I}
2	9.28		$\bar{\pi}_{\text{Alk}}$
3	9.84		n_{I}

^a Vibrational spacings may be in error by ± 150 cm^{-1} . ^b The notation of the MOs of the allenes 1-4 refer to those introduced in the text (for more details cf. ref 3b, 5a).



= 0.51 eV) between bands 1 and 2 corresponds to that of 10^+ ($\Delta = 0.52$ eV).^{19a}

For 5^+ the split between bands 1 and 2 and the shape of the two bands (including vibrational fine structure) are understood in terms of the Cederbaum treatment²⁰ as a result of vibronic coupling (here, in particular, Jahn-Teller distortion of 5^+). Correspondingly, the shape of the two lowest energy PE bands of 10^+ can be ascribed to a pseudo-Jahn-Teller distortion of the radical cation resulting from the accidental degeneracy of the two highest energy (occupied) orbitals in the neutral molecule 10. According to Cederbaum, substitution diminishes effects of vibronic coupling^{20b} which explains qualitatively the differences in the shapes of the PE spectra of 5^+ and 10^+ . The similarity in the general features of bands 1 and 2 in the dialkyl compounds 1^+ and 10^+ suggests an interpretation of the PE spectrum of 1^+ in line with the above elaborations. Following Heilbronner^{19a} we assume that the first maximum (e_1 , Table I) of the Jahn-Teller band couplet corresponds more closely to the Koopmans' value of the degenerate orbital than the second one.

Generally, for the lowest energy PE bands of methylated allenes different vibrational progressions (1050-1150 and 1600-1700 cm^{-1}) are observed, depending upon the substitution pattern of the molecules.^{19a} In the PE spectrum of 10^+ (and other rotationally symmetric methylallenes) ~ 1100 cm^{-1} vibrational progressions have been detected. Though for 1^+ the observed vibrational progressions of 400-500 cm^{-1} (deduced from low-resolution spectra) will have considerable errors, it can be concluded that the vibrational progressions of bands 1 and 2 of 1^+ are different from those of 10^+ . We tentatively attribute the vibrational modes of 1^+ to C=C=C skeletal bendings ($\nu = 356.3$ cm^{-1} in 5^+ ; $\bar{\nu} = 555$ (a') and 322 cm^{-1} (a'') in methylallene (11)²²).

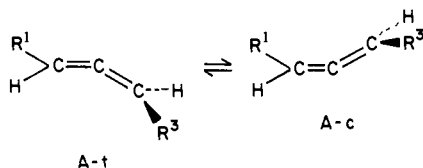
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(20) (a) Köppel, H.; Cederbaum, L. S.; Domcke, W.; Shaik, S. S. *Angew. Chem.* **1983**, *95*, 221. (b) For radical cations the extent of vibronic coupling between two electronic states is determined by the energy gap between them and the vibronic coupling constant λ . λ is related to the LCAO coefficients for the skeletal atoms to which the substituents are attached. Hence, vibronic coupling becomes smaller with increasing mesomeric abilities of the substituents, and geometries of substituted radical cations deviate less from the geometries of the corresponding neutral molecules than in the case of the unsubstituted (parent) cation.^{20a}

For higher energies the PE spectrum of **1** is characterized by heavily overlapping bands which result mainly from ionizations of orbitals comprising the $\text{C}=\text{C}(\text{CH}_3)_3$ moiety. From analogy with 3,3-dimethylbut-1-ene (**9b**) ($\sigma_1((\text{CH}_3)_3\text{C}-\text{C}) = 11.2 \text{ eV}$)²³ band 3 of **1**⁺ is associated with the ejection of an electron from a $\text{C}-\text{C}$ $\text{sp}^2\text{-sp}^3$ σ -bond orbital. The PE spectra of the halogenoallenes **2-4** exhibit almost constant splits ($\Delta = 0.50\text{--}0.55 \text{ eV}$) of the two lowest energy bands, 1 and 2. The shapes of bands 1 and 2, however, are markedly different. The chloroallene **2** shows broad features of two partly overlapping bands of similar intensities with distinct vibrational structures, whereas the iodo compound **4** exhibits two well-separated, sharp bands 1 and 2 (with only slight indications of vibrational progressions). For **4**⁺, band 2 is less intense than band 1. The bromoallene **3** takes an intermediate position. Bands 1 and 2 of **3**⁺ are of similar intensities. They are broader than those of **4**⁺, but they remain as two separated bands which are connected by a small structured hump. Bands 1 of **2**⁺ and **3**⁺ are characterized by the positions of the fine-structure maxima. The sharp bands 3 are generally the most intense ones of the halogenoallenes, and only for **2**⁺ does band 3 show a vibrational structure. This, however, may be due to the fact that for **2**⁺ band 3 should be a superposition of two PE bands, one corresponding to band 3 of **1**⁺ (which exhibits vibrational progressions).

Assuming a 20–30% reduction of the vibrational energies of the neutral molecules upon ionizations, the vibrational progressions of bands 1 of the chloro- and bromoallenes **2** and **3** ($\bar{\nu}^+(2) = 390 \text{ cm}^{-1}$; $\bar{\nu}^+(3) = 400 \text{ cm}^{-1}$) can be associated with either $\text{C}=\text{C}=\text{C}$ skeletal deformations as in **1**⁺ ($\bar{\nu}(6a) = 592 \text{ (a')}, 548 \text{ (a'')} \text{ cm}^{-1}$; $\bar{\nu}(7a) = 603 \text{ (a')}, 519 \text{ (a'')} \text{ cm}^{-1}$)²⁴ or $\text{C}-\text{X}$ bendings ($\bar{\nu}(6a) = 494 \text{ (a') cm}^{-1}$; $\bar{\nu}(7a) = 423 \text{ (a') cm}^{-1}$).²⁴ A second progression observed in band 1 of **3**⁺ ($\bar{\nu}^+ = 910 \text{ cm}^{-1}$) is assigned to the symmetric $\text{C}=\text{C}=\text{C}$ stretching mode ($\bar{\nu}(7a) = 1078 \text{ cm}^{-1}$).²⁴ On the basis of this last observation of an excitation of vibrations in the $\text{C}=\text{C}=\text{C}$ moiety, we attribute the vibrational modes of bands 1 in **2**⁺ and **3**⁺ to $\text{C}=\text{C}=\text{C}$ skeletal bending modes. In this way along the series **1-3** we have a similarity in the vibrational pattern of bands 1 and in the geometry changes of the molecules upon ionizations of the HOMOs (bending of the allenic skeleton).

Bending of the $\text{C}=\text{C}=\text{C}$ moiety in 1,3-disubstituted allenes (**A**) or their ions, however, makes the PE (and also excitation) spectra rather complicated, as such a motion may lead to equilibria of cisoid (**A-c**) and transoid (**A-t**) forms having different energies.



Similar problems are associated with torsional motions of 1,3-disubstituted allenes (**A**) (cf. ref 7a). The torsional mode is fundamental in the Jahn-Teller effect of **5**⁺.²⁰ As vibrations excited in PE spectra usually correspond to motions of the atoms in that part of the molecule where the ionized electron is most heavily localized, the above results indicate that the HOMOs π_X (corresponding to bands 1) of the chloro- and bromoallenes **2** and **3** largely retain their allenic character. The lack of a corresponding vibrational structure of band 1 for the iodo compound **4** is then interpreted as a more marked admixture of heteroatom character into the HOMO; i.e., π_1 should be a mixture of the corresponding group orbitals of the $\text{C}=\text{C}=\text{C}$ and **I** moieties.^{5a}

The loss of vibrational structure of bands 1 and 2 in the iodo compound **4** is in agreement with the Cederbaum theory.^{20a}

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Table II. Calculated Ionization Energies^a of *tert*-Butylallenes ($(\text{CH}_3)_3\text{CCH}=\text{C}=\text{CHX}$ (in eV))

compd	X	$\bar{I}_v(\pi_X)$	$\bar{I}_v(\pi_{\text{Alk}})$
1	$(\text{CH}_3)_3\text{C}$	8.93 ^b	8.93 ^b
2	Cl	9.20	9.78
3	Br	9.09	9.61
4	I	8.67	9.63

^aEquation 3. ^b e_1 in Table I.

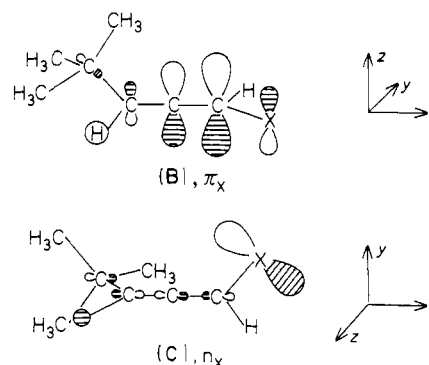


Figure 3. Symbolizations of the delocalizations of π_X and n_X orbitals in (*S*)-*tert*-butylallenes through hyperconjugations.

Accordingly, increased delocalizations of orbitals lead to diminished vibronic coupling.^{20b} As delocalization of the π_X orbital across the $\text{C}=\text{C}=\text{C}$ and **X** moiety increases in the series $\text{Cl} < \text{Br} < \text{I}$, effects of vibronic coupling should decrease for **4**⁺ < **3**⁺ < **2**⁺.

Since the PE spectra of monosubstituted allenes (**6a**, **7a**)^{5a} and ethylenes (**6b-8b**)^{23,25} are known, the PE band assignments given in Table I could utilize energetical criteria referring to an additivity model of substituent effects on the two highest energy orbitals of 1,3-disubstituted allenes (**A**).^{3b} According to this model ($\text{R}^3 = \text{X}$) the theoretical (vertical) ionization energy \bar{I}_v of π_X and π_{Alk} is given by eq 3 with the substituent parameters β and μ being

$$\bar{I}_v(\pi_X) = 10.07 + \beta(\text{X}) + \mu(t\text{-Bu}) \quad (3a)$$

$$\bar{I}_v(\pi_{\text{Alk}}) = 10.07 + \beta(t\text{-Bu}) + \mu(\text{X}) \quad (3b)$$

defined in ref 3b.^{26b} With eq 3 one obtains theoretical values for the ionization energies that, with the exception of $\bar{I}_v(\pi_{\text{Alk}})$ for **4**, agree within $\pm 0.15 \text{ eV}$ with the experimental ones (Table II). Hence, in **2-4**, band 1 correlates with $\pi_X(a')$ in **6a-8a**, band 2 correlates with $\pi(a')$ in **6a-8a**, and $\pi_X-\pi_{\text{Alk}}$ mixing effects should have only little influences on orbital energies or ionization energies, respectively, of **2-4**.

The sharp PE bands 3 of **2**⁺-**4**⁺ obviously correspond to ionizations of the halogen lone pairs n_X (which lie in the plane defined by the CHX grouping). Interestingly, in **2-4** the n_X orbitals are destabilized by 0.30–0.35 eV relative to those of the monosubstituted compounds **6a-8a**.

The interactions of the substituents with the allenic skeleton have been discussed in detail in ref 4 and 5a. Therefore, in this work attention should be focused on the information about ion-

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(26) (a) Ionization energies of the monosubstituted allenes **8a** and **9a** are not reported in the literature. From the correlations given in ref 4 and 5a, however, one can estimate the following ionization energies: 9.0 (π), 10.4 (π), and 10.1 eV (n_1) for **8a** and 9.3 (π) and 9.7 eV (π) for **9a**. (b) The additivity model is based on substituent effects $\beta(\text{R})$ and $\mu(\text{R})$ on $\pi(a')$ and $\pi(a'')$ orbitals in monosubstituted allenes ($\beta(\text{R}) = -10.07 + I_v(\pi)$ and $\mu(\text{R}) = -10.07 + I_v(\pi)$).^{3b,4} In this way, one has the following:^{4,5a,26}

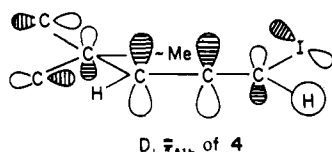
	<i>t</i> -Bu	Cl	Br	I
$\beta(\text{R}), \text{eV}$	-0.77	-0.50	-0.61	-1.07
$\mu(\text{R}), \text{eV}$	-0.37	+0.48	+0.31	+0.33

The additivity model should be valid for 1,3-disubstituted allenes, if $\pi-\pi$ mixing effects are relatively small.^{3b,4}

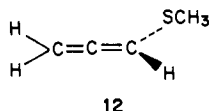
teractions of the substituents across the allenic skeleton, which can be inferred from the PE data. The first point of interest in this context is the destabilization of the HOMOs π_X of **2** and **3** relative to the π (a'') orbitals of monosubstituted allenes **6a** and **7a^{5a}** by 0.27 and 0.36 eV, respectively. According to the model presented in ref 4 and 5a, the electric group dipole moment of the *tert*-butyl group ($\bar{\mu}(t\text{-Bu}) \approx 0.9$ D)^{5a} (attached to the γ site of $\text{H}_2\text{C}=\text{C}=\text{CHX}$) will destabilize the HOMO $\pi_X(a'')$ by no more than 0.20–0.25 eV, if only Coulombic interactions through space were operative. The larger destabilizations of π_X in the present molecules (especially π_{B} , by 0.36 eV) hint at an additional effect. This could be a contribution due to a pseudo-Jahn-Teller split of the close lying orbitals π_X and $\bar{\pi}_{\text{Alk}}$. As has been discussed, vibronic coupling should be rather small in the halogenoallenes **3** and **4**. Therefore, we suggest attributing the additional destabilization of π_X in **2–4** primarily to a “hyperconjugation” involving the *tert*-butyl group similar to that detected for γ -substituted phenylallenes by ¹³C NMR spectroscopy.¹ This hyperconjugation is schematically depicted by B in Figure 3.

Hyperconjugation of the type B involving an alkyl group can also be inferred from the LCAO expansions of the outermost orbitals of ethylallene ($\text{CH}_3\text{CH}_2\text{CH}=\text{C}=\text{CH}_2$) within the semiempirical CNDO/S or ab initio STO-3G scheme.⁵ In B the orbital π_X retains largely the nodal plane of the correlated orbital $\pi(a'')$ of monosubstituted allenes. It cannot be ruled out, however, that an admixture of $\bar{\pi}_{\text{Alk}}$ into π_X according to eq 1a operates as a further factor that induces the enlarged destabilization of π_X in **2–4**.

Correspondingly, one may expect hyperconjugative interactions to be operative in the $\bar{\pi}_{\text{Alk}}$ orbital. Marked $\bar{\pi}_{\text{Alk}}/n_X$ hyperconjugation should be found for the iodo compound **4**. It is diagrammed in D (Me = CH_3). A similar, strong $\bar{\pi}/n_X$ interaction (X =



SCH_3) is observed in the PE spectrum²⁷ of methyl allenyl sulfide (**12**) and corroborated by quantum-chemical calculations.^{5b,6} For



X = Cl or Br the $\bar{\pi}_{\text{Alk}}/n_X$ interactions will be much smaller (or even negligible). The reason for the nonnegligible $\bar{\pi}_{\text{Alk}}/n_X$ hyperconjugation is surely due to the relatively small energy gap of ~ 1.1 eV between the “unperturbed” orbitals $\bar{\pi}_{\text{Alk}}$ (–9.3 eV) and n_X in case of X = I ($n_I \approx -10.4$ eV). For X = Cl or Br, however, the gap exceeds 2.4 eV ($n_{\text{Br}} \approx -11.7$ eV, $n_{\text{Cl}} \approx -12.7$ eV).⁴

The almost constant splitting of ca. 0.5 eV of the two low-energy PE bands of **1–4** seems to be coincidental due to a number of (above mentioned) substituent effects on orbital energies and varying extents of vibronic coupling effects.

The destabilizations of the n_X orbitals in **2–4** by 0.22–0.34 eV relative to those in **6a–8a^{5a,26a}** are tentatively attributed to a combined effect which results from the influence of the *tert*-butyl group's dipole moment (“field effect”) and a (overlap-dependent) hyperconjugative effect. This leads to certain delocalizations of the n_X orbitals in **2–4** as given in Figure 3 (C). Due to the large distance ($r \approx 5$ Å) between $\bar{\mu}(t\text{-Bu})$ and the n_X orbital which is centered largely at the heteroatom the field effect of the *tert*-butyl group is presumably less important.

2. Near-Ultraviolet Circular Dichroism and Absorption Spectra. The solution UV absorption and CD spectra of **1–4** are displayed

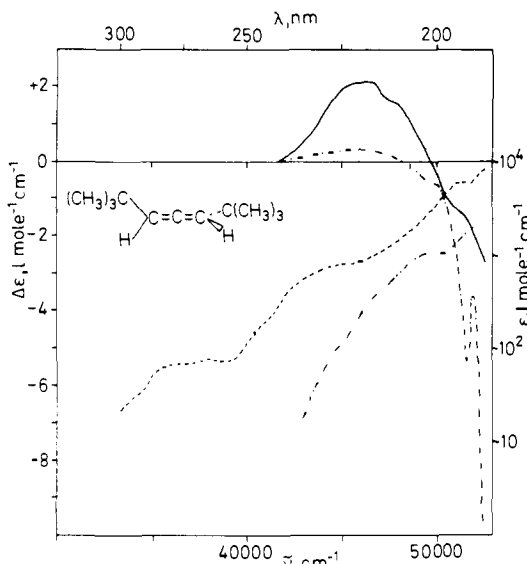


Figure 4. Near-ultraviolet absorption and CD spectra of 1,3-di-*tert*-butylallene (**1**): (—) CD, isooctane; (---) CD, gas phase; (---) UV, *n*-hexane; (---) UV, gas phase.

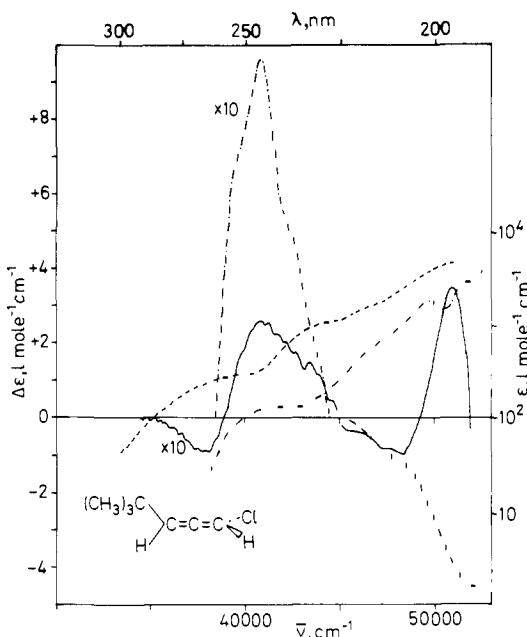


Figure 5. Near-ultraviolet absorption and CD spectra of 1-chloro-4,4-dimethyl-1,2-pentadiene (**2**): (—) CD, isooctane; (---) CD, gas phase; (---) UV, *n*-hexane; (---) UV, gas phase.

in Figures 4–7. For the discussion of the near-ultraviolet electronic spectra of **1–4** (spectral range 300–195 nm) emphasis will be on the solution spectra. Comparisons with the gas-phase spectra in that spectral range will be mainly used to inquire further into the nature of the electronic transitions which are responsible for the electronic bands in the condensed phase.

(*R*)-1,3-Di-*tert*-butylallene (**1**) exhibits an apparent simple solution CD spectrum (Figure 4) with one relatively strong positive band having a maximum at 46 300 cm^{-1} and an inlet near 48 000 cm^{-1} . Toward the blue region the CD changes its sign and a further inlet near 51 000 cm^{-1} is observed. The 46 300 cm^{-1} CD band has a corresponding medium intense shoulder (ϵ 590) in the absorption spectrum. The absorption spectrum, however, reveals two additional features that cannot be observed in the CD. At 37 900 cm^{-1} a weak UV band with 1200- cm^{-1} vibrational progressions is found, and at 51 300 cm^{-1} the UV spectrum exhibits a hump. A $\sim 1100\text{-cm}^{-1}$ vibrational progression is also observed for the lowest energy UV band ($\bar{\nu} = 38\,500\text{ cm}^{-1}$) of (*tr*-

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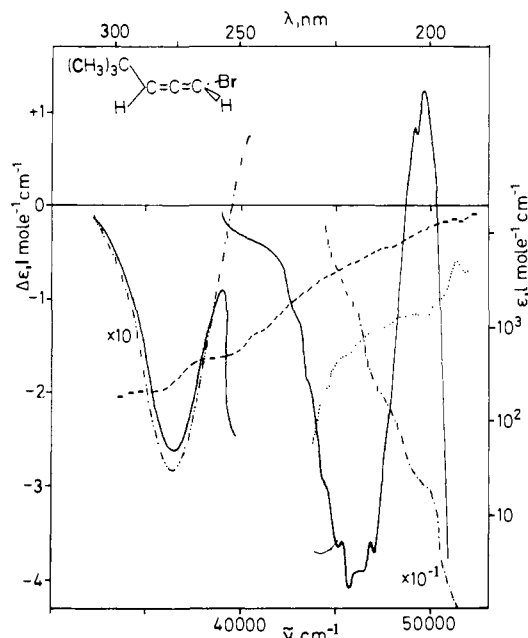


Figure 6. Near-ultraviolet absorption and CD spectra of 1-bromo-4,4-dimethyl-1,2-pentadiene (**3**): (—) CD, isoctane; (---) CD, CCl₄; (-·-·) CD, gas phase; (---) UV, *n*-hexane; (···) UV, gas phase.

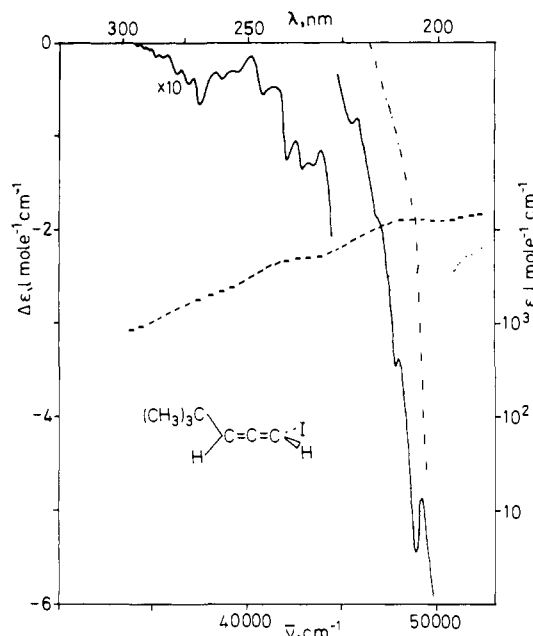
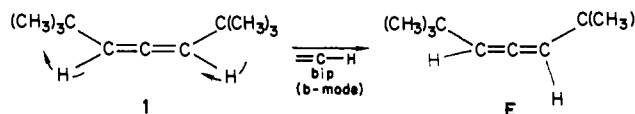


Figure 7. Near-ultraviolet absorption and CD spectra of 1-iodo-4,4-dimethyl-1,2-pentadiene (**4**): (—) CD, isoctane; (---) CD, gas phase; (---) UV, *n*-hexane; (···) UV, gas phase.

methylsilyl)allene ((CH₃)₃SiCH=C=CH₂; ref 80 in ref 5a). The 1200-cm⁻¹ vibrational progression of the 37 900-cm⁻¹ UV band of **1** is tentatively associated with one of the (symmetric (a) or antisymmetric (b) combinations of the =C—H bendings in the plane ("bip") ($\bar{\nu}(\text{=C—H}) = 1327 \text{ cm}^{-1}$ in **11**)²² as shown, for instance, in E. Compound **1** has a solution CD spectrum which

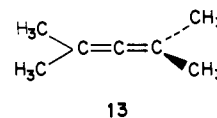


is very similar to that of (*R*)-(-)-1,3-dimethylallene (**10**).^{7a} In ref 7a the positive CD band of **10** at 48 400 cm⁻¹ is assumed to correspond to the lowest excited singlet state of the allene chromophore (¹A₂). This assignment is simultaneously used as a basis

for a theoretical discussion of the optical activity of the allene chromophore.^{7a} However, the 48 400-cm⁻¹ CD band of **10** definitely does not correspond to the ¹A₂ excited state. Detailed analyses and correlations among excited states (and their energies) of simple allenes have revealed that the bands corresponding to the lowest energy excited states of the allene chromophore should be observed in the range 36 000–42 000 cm⁻¹, whereas those corresponding to ¹B₁ should be found in the range 42 000–49 000 cm⁻¹.³ For these reasons the weak 37 900-cm⁻¹ UV absorption band of **1** (which has no corresponding CD band) is associated with the (intravalance) excited state ¹A₂ and the 46 300-cm⁻¹ band with ¹B₁. Relative to the gas-phase spectrum of **1** (Figure 4) the positive CD maximum persists in solution. This confirms the valence-shell character of the transition leading to the 46 300-cm⁻¹ band. Recent ab initio calculations suggest^{7b} that the lowest energy ¹A₂ and ¹B₁ excited states of the allene chromophore have considerable Rydberg character. Our observations, at least with respect to the ¹B₁ band, are at variance with this proposal.

In general, for open-chain alkylallenes no CD can be detected in the energy region where the excited state ¹A₂ (in *D*_{2d} or *C*₂ allenes)^{7a,28} or the correlated ¹A'' state (in *C*_s allenes)³⁰ are expected. In the allenic *D*_{2d} chromophore²⁹ (or allenic *C*_s chromophore²⁹) the excited state ¹A₂ (or ¹A''(π,π*), respectively) results from a MA,EF transition. Through distortions the molecule may gain electric transition moments, and hence, one would expect the ¹A₂ (¹A'') excited state to be associated with a distinct CD signal. If the allenic moiety is part of a ring (in the endo position^{7a,31,32} or exo position^{30,31,33}), indeed, a CD band can be observed in the energy range of the ¹A₂ (¹A''(π,π*)) excited state, its sign being opposite to that of the higher energy band (near 46 000 cm⁻¹). Therefore, we interpret the apparent disappearance of the ¹A₂ CD band of **1** (and similar allenes)²⁸ as being due to overlap with the stronger ¹B₁ CD band of opposite sign; i.e., the ¹A₂ CD band is canceled by that of ¹B₁.

Overlap with the higher energy CD band of opposite sign is probably also the reason for the drastic decrease in intensity of the ¹B₁ CD band of the condensed phase as compared with the gas phase (Figure 4). This overlap is seen in the gas-phase absorption spectrum of **1** (Figure 4). In the gas phase the 46 000-cm⁻¹ UV shoulder appears only as an inflection of the onset of a stronger band with a hump at 49 400 cm⁻¹. Comparison with the situation in tetramethylallene (**13**)¹¹ suggests that the



49 400-cm⁻¹ UV hump corresponds to the e₁ → 3s Rydberg transition (cf. section III.3). Changing from the gas phase to the condensed phase shifts this last UV band to 51 300 cm⁻¹, as is expected for a Rydberg band.^{34,35} The observed blue shift of 1900 cm⁻¹ is a little smaller than the shift of the corresponding Rydberg band of **10** (2300 cm⁻¹).^{7a}

A remark concerning the possible mechanism for the origin of the CD of **1** shall complete the discussion of the allenic hydrocarbon. Anticipating vacuum-UV results (section III.3), we can

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show that the signs of the rotatory strengths of **1** are $R(^1A_2) < 0$, $R(^1B_1) > 0$ and $R(^1B_2) < 0$ (and $R(^1A_1) > 0$). Such a sign pattern is predicted on the basis of a dynamic coupling model³³ using electronic states of the allene chromophore that remain unmixed under the perturbation of the (rotationally symmetric) alkyl substituents. In this model the rotational strengths are generated essentially by the electric dipoles induced in the two substituents. Polarizability calculations for **10** using a corresponding model (which dissects the molecule into the allene chromophore and the alkyl ligands) could satisfactorily reproduce the CD of the 1B_2 excited state.¹⁷ Therefore, we assume such models to be appropriate to describe the optical activity of the allenic chromophore. This means that, in agreement with Zandomeneghi,¹⁷ one may assume that the interpretation of the circular dichroism does not require an intrinsically dissymmetric chromophore, as proposed recently.^{7a}

The first impression looking at the solution UV absorption and CD spectra of the halogenoallenes **2-4** (Figures 5-7) is that the absorption with smoothly rising curves (with some shoulders) contrasts markedly with the CD where several distinct, oppositely signed bands are seen. The CD spectra, furthermore, exhibit characteristic vibrational structures. In **2-4** electronic excitations can be expected to originate with the n_X , π_{Alk} , and π_X orbitals. Valence-shell transitions will terminate at the π^*_X and π^*_{Alk} orbitals. For the halogenoallenes **2-4**, however, excitations involving valence-like d halogen AOs may also be observed, similar to the situation with methyl allenyl sulfide (**12**).⁶ The unoccupied orbital of interest in this regard is the C-X antibonding σ orbital (σ^*_{C-X}) which contains large admixtures from halogen d AOs.^{5a,36} For the chloroallene **2**, four CD bands with energies less than 52 000 cm^{-1} and alternating signs are observed in the solution spectrum (Figure 5). The two lowest energy CD bands are rather weak, whereas the higher energy CD bands have medium intensities.

Apart from a red shift of the corresponding bands, the CD spectrum of the bromo compound **3** is very similar to that of the chloroallene **2** (Figure 6). The major deviations are the loss of vibrational structure of the lowest energy CD band (similar to the situation with the PE spectra of **2** and **3**) and the apparent disappearance of the positive CD band near 41 000 cm^{-1} . It seems, however, that **3** has a positive CD band near 41 000 cm^{-1} which is canceled by the subsequent strong CD band of opposite sign. This is indicated when the CD spectrum of **3** is run in CCl_4 (Figure 6). In that solvent the CD becomes positive after 40 000 cm^{-1} . Further support for the existence of an electronic band near 41 000 cm^{-1} comes from the solution UV spectrum of **3** (Figure 6), where at the corresponding position an inflection is found. Finally, in Figure 8 the CD spectrum of **2** has been superimposed on that of **3** such that the CD maxima of the highest and lowest energy bands come into coincidence. This picture gives a clear indication how the 41 000- cm^{-1} CD band of **3** may be canceled by the subsequent strong one of opposite sign.

Considering all this one can be quite sure that the bromoallene has an electronic transition near 41 000 cm^{-1} . All four bands in **2** and **3** are assumed to correspond to different excited states S_1-S_4 (with energies $\bar{\nu} = 38\,170$, 40 780, 48 540, and 51 020 cm^{-1} for **2** and $\bar{\nu} = 36\,400$, 41 000, 45 660, and 49 650 cm^{-1} for **3**). The energy separations between S_1 and S_2 in **2** and **3** (and S_3 , S_4 in **2**) are rather small so that vibronic coupling effects may be anticipated.

The vibrational progressions of the 45 660- and 49 650- cm^{-1} CD bands of the bromoallene **3** ($\bar{\nu} = 550$ and 510 cm^{-1} , respectively) should correspond to the C-Br stretching vibration ($\bar{\nu}_{C-Br} = 681$ cm^{-1} in **7a**).²⁴ A second progression of the former band (S_3 , $\bar{\nu} = 900$ cm^{-1}) is attributed to the symmetric C=C=C stretching mode ($\bar{\nu} = 1078$ cm^{-1} in **7a**).²⁴ The corresponding 48 540- cm^{-1} CD band (S_3) of the chloroallene **2** has 800- cm^{-1} vibrational progressions which, probably, can be associated with the C=C=C stretch ($\bar{\nu} = 1101$ cm^{-1} in **6a**).²⁴ For the vibrational spacings of the lowest energy CD band of **2** ($\bar{\nu} = 360$ cm^{-1}), two alternatives are possible. Either it corresponds to C=C=C bending ($\bar{\nu} = 592$ (a'), 548 (a'') cm^{-1} in **6a**),²⁴ which seems also

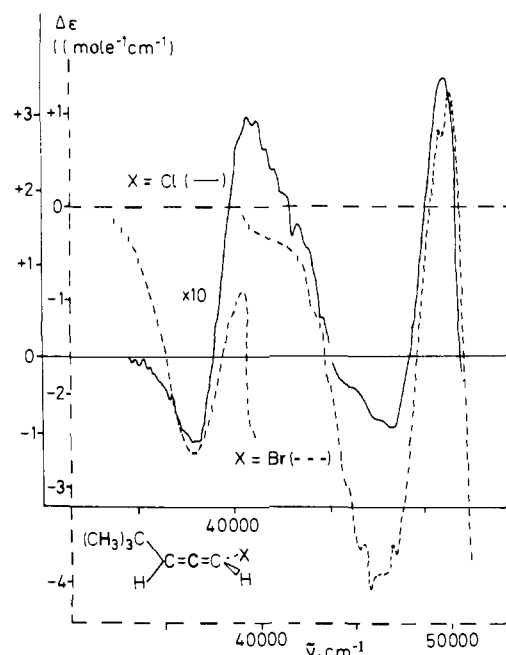
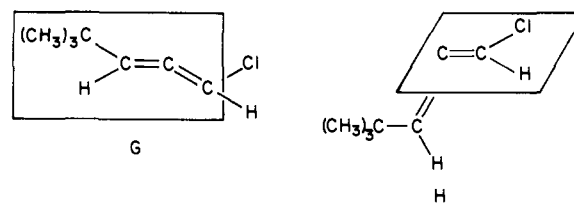


Figure 8. Superposition of the CD spectra of chloro- and bromoallenes.

to be operative in the lowest energy PE band of **2**, or it corresponds to in-plane C=C-Cl bending ($\bar{\nu} = 494$ cm^{-1} in **6a**).²⁴ The progression of the 40 780- cm^{-1} CD band (S_2) of **2** ($\bar{\nu} = 480$ cm^{-1}) corresponds with high probability to C=C=C bending since the C=C-Cl bending frequency should be reduced in the excited state to 350-400 cm^{-1} . We suggest that the vibration in the lowest energy electronic excitation (S_1) of **2** is also C=C=C bending. The C=C-Cl bending is ruled out, because the outermost (occupied and unoccupied) π_X and π_{Alk} orbitals of **2** are to a large extent localized at the allenic moiety; i.e., π_{Cl} has only a little electron density in the C-Cl region (Figure 3). The 480- cm^{-1} vibration of the second band of **2** obviously must involve the bending of the C=C=C entity in the *t*-BuCH plane ($\bar{\nu}(a') = 555$ cm^{-1} in **11**)²⁴ as visualized in G. On the other hand, the 360- cm^{-1}



progression of the first band (S_1) of **2** should correspond to the C=C=C bending vibration of lower energy, i.e., the one out of the ClCH plane (H). This, however, means that the gross geometrical changes associated with the two lowest energy excitations (S_1, S_2) are identical (G = H).

Bending of the C=C=C skeleton is assumed to be a prerequisite for the generation of optical activity of 1,3-dialkylallenes, such as **10**.^{7a} Hence, the above observations seem to indicate that the model suggested in ref 7a is adequate, at least for certain cases. In our view, however, the geometry distortion induced by C=C=C bending in **2** is associated with a (accidental) degeneracy of the two lowest excited singlet states of **2** and vibronic coupling ("pseudo-Jahn-Teller distortion") through C=C=C bending. A corresponding (bending) distortion in the excited state is also observed for carbon dioxide, O=C=O.^{20a}

As the second CD band of **2** is not affected by changing the gas phase to the condensed phase, the valence-shell character of the corresponding electronic transition is demonstrated. In absorption the two lowest energy transitions of **2** and **3** have low UV intensities; i.e., both should result from electric dipole forbidden transitions. Comparisons with assignments given for **6a**

and $7a^{3,5a}$ and other allenes^{3b} suggest that the above transitions are associated with excited states S_1 and S_2 having electronic configurations $(\pi_X, \bar{\pi}^*_{Alk})$ and $(\bar{\pi}_{Alk}, \pi^*_X)$, respectively, as their leading terms.

The high-energy absorption bands (S_4) of **2** and **3** are rather intense and should correspond to electric dipole allowed transitions. In **3** the vibrational structure of the S_4 CD band ($\bar{\nu} = 510 \text{ cm}^{-1}$), which has been related to the C-Br stretching mode ($\nu_{C-Br} = 681 \text{ cm}^{-1}$), indicates that the electronic excitation involves the C-Br moiety of the molecule. The low-energy orbitals with sufficiently large electron densities in the C-Br region are n_{Br} , π_{Br} , π^*_{Br} , and σ^*_{C-Br} . The only combinations resulting in EA transitions (in the C_3 allene **7a**) are (π_{Br}, π^*_{Br}) and $(n_{Br}, \sigma^*_{C-Br})$. As the (π_{Br}, π^*_{Br}) transition is found in the vacuum-ultraviolet spectrum, the 49 650- cm^{-1} CD band (S_4) of **3** should involve the $(n_{Br}, \sigma^*_{C-Br})$ excitation. Correspondingly, in **2** the 51 020- cm^{-1} CD band (S_4) should be associated with the $(n_{Cl}, \sigma^*_{C-Cl})$ transition.

As the vibrational structures of S_3 in **3** (C-Br and C=C=C stretching) indicate excitations in the C=C=C and C-Br moieties, (π_X, σ^*_{C-X}) are appropriate candidates for the corresponding transitions. These last excitations correlate with the weak $N \rightarrow Q$ ($n\pi, \sigma^*_{C-X}$) transitions in CH_3X (which are observed at 58 000 cm^{-1} for $X = Cl$, and 50 000 cm^{-1} for $X = Br$).³⁶⁻³⁹ The band assignment presented for **2** and **3** on the basis of empirical evidence is exactly that predicted for chloroallene **6a** with the semiempirical CNDO/S scheme if chlorine 3d AOs are included.^{5a} According to these calculations,^{5a} S_4 involves $(n_{Cl}, \sigma^*_{C-Cl})$ and a small admixture from the (n_{Cl}, σ^*) excitation where σ^* comprises essentially carbon 2s and allenic hydrogen 1s AOs (and correlates with the lowest energy nondegenerate unoccupied orbital ($5a_1$) in **5**).

Referring to the gas-phase CD spectra (Figures 5 and 6), where S_3 appears as a shoulder of a stronger negative CD band, one can see that S_3 persists in the condensed phase. This demonstrates the intravalence character of S_3 . On the other hand, there are no correspondences for the high-energy positive CD bands (S_4) of **2** and **3** in the gas phase. We tentatively interpret this observation as caused by a blue shift of the S_4 CD band in the vapor phase which makes S_4 overlap with the very strong higher energy CD bands of opposite signs (III.3).

On comparison of the gas-phase and condensed-phase UV absorption spectra of **2** and **3** (Figures 5 and 6) for the chloro compound **2** no great differences are observed. A hump at 49 630 cm^{-1} and a shoulder near 51 600 cm^{-1} in the gas phase disappear in the solution spectrum of **2**. Referring to the red shift of EA valence-shell transitions in solution, the 49 630- cm^{-1} gas-phase hump is related to the 48 000- cm^{-1} (CD) band in solution (S_3). The shoulder near 51 600 cm^{-1} has a pronounced negative CD with a maximum at 52 630 cm^{-1} (cf. Figure 10) which cannot be S_4 (with a positive CD in solution). Hence, we attribute the 52 630- cm^{-1} feature in the gas phase to a Rydberg transition.

For the bromoallene **3** a sharp peak at 51 280 cm^{-1} in the gas phase seems to correspond to a small hump in the solution absorption spectrum at the same position. Comparing the rise of intensity of the gas-phase UV spectrum of **3** after 50 000 cm^{-1} with that of the solution spectrum, one may conclude that the 51 280- cm^{-1} gas-phase and solution UV bands stem from different band systems. The hump in the solution spectrum probably is part of the S_4 band. The sharp 51 280- cm^{-1} peak should correspond to a Rydberg transition.

In the solution UV spectrum of the iodoallene **4** (Figure 7) three shoulders at 37 000, 42 000, and 48 600 cm^{-1} indicate the existence of at least three different excited states with energies less than 50 000 cm^{-1} . The solution CD spectrum of **4** (Figure 7) reveals distinct vibrational structures of the electronic bands. The UV

shoulder at 48 600 cm^{-1} appears in the CD as a system of vibrational components superimposed on the onset of a very strong CD band with the same sign. Its 900- cm^{-1} vibrational progression should correspond to the symmetric C=C=C stretching mode ($\bar{\nu} = 1076 \text{ cm}^{-1}$ in **8a**),²⁴ similar to the situations in **2** and **3**. The 560- cm^{-1} progression of the 42 000- cm^{-1} band may be attributed to C=C=C bending ($\bar{\nu} = 625$ (a') cm^{-1} in **8a**)²⁴ or to the C-I stretching vibration ($\bar{\nu} = 609 \text{ cm}^{-1}$ in **8a**).²⁴ Comparisons with the situation in the bromoallene **3** suggest the 560- cm^{-1} mode to be associated with C-I stretch, and furthermore, the last two electronic bands of **4** should result from the (n_1, σ^*_{C-I}) excitation (S_4 , 48 600 cm^{-1}) and the (π_1, σ^*_{C-I}) excitation (S_3 , 42 000 cm^{-1}). The involvement of the symmetric C=C=C stretching vibration in the (n_1, σ^*_{C-I}) transition can be rationalized by the PE data, i.e., the partial delocalization of the n_1 orbital of **4** (Figure 3, C). From analogy with the other haloallenes (**2** and **3**), one may expect that the low-energy parts of the electronic spectra of **4** are governed by two transitions, $(\pi_1, \bar{\pi}^*_{Alk}) \approx S_1$ and $(\bar{\pi}_{Alk}, \pi^*_1) \approx S_2$. In the relevant spectral range, however, apparently only one (negative) CD band exists. In the low-energy part, this "band" exhibits a 360- cm^{-1} vibrational progression, as S_1 in **2**, whereas toward the blue region the vibrational progression is 580 cm^{-1} . This last progression should correspond to C=C=C bending in the HCl plane ($\bar{\nu} = 625 \text{ cm}^{-1}$ in **8a**),²⁴ i.e., the bending modes correspond to those displayed for **2** in G and H. In analogy with the observation for the bromo compound **3** (Figure 8), we assume that **4** has two electronic transitions with energies less than 42 000 cm^{-1} which are vibronically coupled and generate the lowest energy CD "band" of **4**. The shape of that band results from vibronic coupling effects and an overlap of a positive band S_2 (with a maximum at 40 160 cm^{-1} , which corresponds to the point having the smallest $|\Delta\epsilon|$ value) with two neighboring CD bands of opposite signs. Then, this band (S_2) is attributed to an excitation with a $(\bar{\pi}_{Alk}, \pi^*_1)$ leading term and the one of lowest energy (S_1 , 37 410 cm^{-1}) to $(\pi_1, \bar{\pi}^*_{Alk})$.

In the gas-phase CD spectrum of **4** the vibrational structure of the 48 600- cm^{-1} condensed-phase band disappears. Referring to the disappearances of the S_4 CD bands of **2** and **3** and their interpretations, it is suggested that also for **4** S_4 is shifted markedly to the blue region going from the condensed phase to the vapor phase. Hence, it will be buried by the higher energy CD bands. For this reason it is clear that the band observed at ca. 49 000 cm^{-1} in the gas-phase UV spectrum of **4** cannot correspond to S_4 (III.3).

As a summary, it has turned out that the lower excited valence-shell transitions (with energies less than 52 000 cm^{-1}) of the haloallenes **2-4** have very similar energies. The two lowest excited states (S_1 and S_2) are vibronically coupled. The chloro and iodo compound (**2** and **4**) have bent excited-state geometries, whereas for the bromoallene no information about the geometries of S_1 and S_2 can be inferred. The excited states S_1 and S_2 of **2-4** result largely from excitations localized at the allenic skeleton, as the involved orbitals π_X , π^*_X , $\bar{\pi}_{Alk}$, and $\bar{\pi}^*_{Alk}$ are mainly allene-type orbitals. When normalization constants and λ being much smaller than one are neglected, the two lowest excited states should be described according to $[(\pi_X, \bar{\pi}^*_{Alk}) - \lambda(\bar{\pi}_{Alk}, \pi^*_X)]$ (S_1) and $[(\bar{\pi}_{Alk}, \pi^*_X) + \lambda(\pi_X, \bar{\pi}^*_{Alk})]$ (S_2) (cf. Table IV). Hence, S_1 and S_2 of **2-4** are similar in character to 1A_2 and 1B_1 of the allenic hydrocarbon **1**. On the other hand, S_3 and S_4 are associated with the halogen atoms of **2-4** and can only be rationalized if halogen valence-like d AOs are taken into account. The excitations leading to S_3 and S_4 terminate at the antibonding σ^*_{C-X} orbital which contains d AOs in its LCAO expansion.

Finally, as noted by Rauk^{7a} the 1A_2 (S_1) and 1B_1 (S_2) valence excited states of allene (**5**) are lowered by twisting and bending. Recent calculations by Johnson^{7d} also show this effect. For small deformations of the antipolar allenic geometry the sequence $^1A_2 < ^1B_1$ is retained. Upon continuous rotation or rotation bending motions, however, crossing of 1A_2 and 1B_1 occurs and two excited state minima (correlating with 1B_1) are reached at planar (achiral) geometries.^{7d}

In an attempt to discuss qualitatively the role of nonvertical

(36) (a) Russell, B. R.; Edwards, L. O.; Raymond, J. W. *J. Am. Chem. Soc.* **1973**, *95*, 2129. (b) Raymond, J. W.; Edwards, L. O.; Russell, B. R. *J. Am. Chem. Soc.* **1974**, *96*, 1708.

(37) Causley, G. C.; Russell, B. R. *J. Chem. Phys.* **1975**, *62*, 848.

(38) (a) Haszeldine, R. N. *J. Chem. Soc.* **1953**, 1764. (b) Boschi, R. A.; Salahub, D. R. *Mol. Phys.* **1972**, *24*, 289.

(39) Gedanken, A.; Rowe, M. D. *Chem. Phys. Lett.* **1975**, *34*, 39.

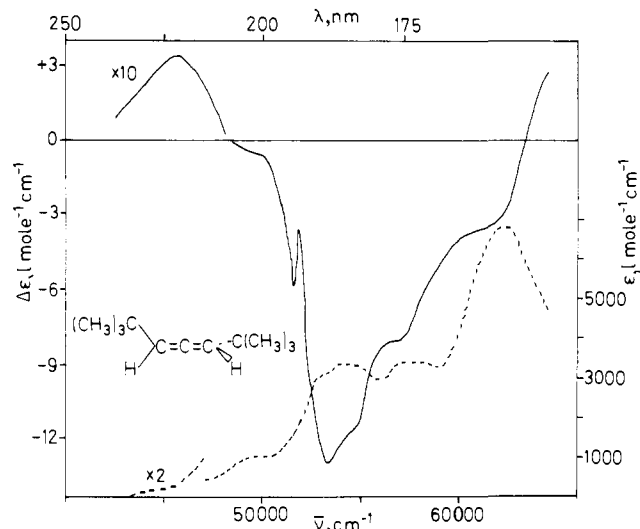


Figure 9. Gas-phase vacuum-UV absorption (---) and CD spectra (—) of 1,3-di-*tert*-butylallene (**1**).

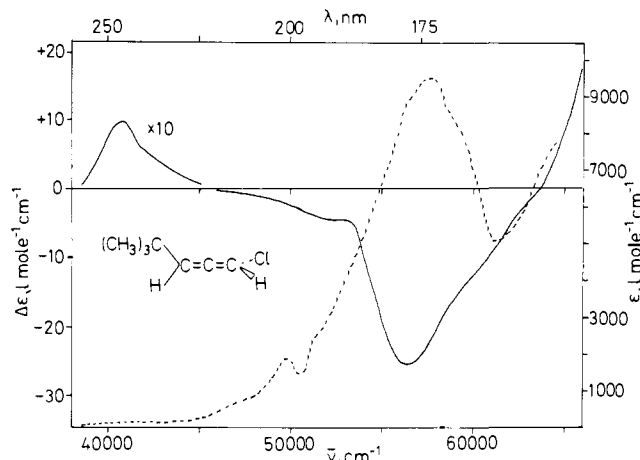


Figure 10. Gas-phase vacuum-UV absorption (---) and CD spectra (—) of 1-chloro-4,4-dimethyl-1,2-pentadiene (**2**).

transitions in the electronic spectra of the allene chromophore one may perhaps reason along the following lines. In **1** at low energy no CD can be detected and continuous absorption begins at $\sim 31\,000\text{ cm}^{-1}$ ($\sim 3.84\text{ eV}$) (which is not displayed in Figure 4). The actual (nonvertical) 0-0 band should have an energy of $\sim 3.8\text{ eV}$ or maybe even lower. The observed rise of absorption probably covers an almost planar excited state with slight deformations from that planar geometry due to a number of (C=C=C and C-H) twisting and bending deformations.

Furthermore, the chloroallene **2** is rather close to **1** in its electronic (orbital and excited states) characteristics. **2** has (C=C=C) bent excited states S_1 and S_2 . In agreement with the analysis of Johnson,^{7d} the larger deformations of the two lowest energy excited states result in convergence of S_1 and S_2 in **2**, the energy gap (2610 cm^{-1}) being much smaller than that of **1** (8400 cm^{-1} , Table IV) where distortion is not so pronounced.

3. Vacuum-Ultraviolet Circular Dichroism and Absorption Spectra. The gas-phase vacuum-UV absorption and CD spectra of **1-4** are shown in Figures 9-12. Contrary to the solution spectra, in the vacuum-UV region the absorption spectra are much more structured than the CD spectra. All four compounds exhibit broad and strongly negative CD bands with maxima between $53\,000$ and $56\,000\text{ cm}^{-1}$. For the CD maxima corresponding absorption maxima are found. Toward the blue region the CD changes its sign and becomes positive between $60\,000$ and $64\,000\text{ cm}^{-1}$.

The investigation of the higher excited states of the allenes **1-4** advantageously starts from the vacuum-UV absorption spectra.

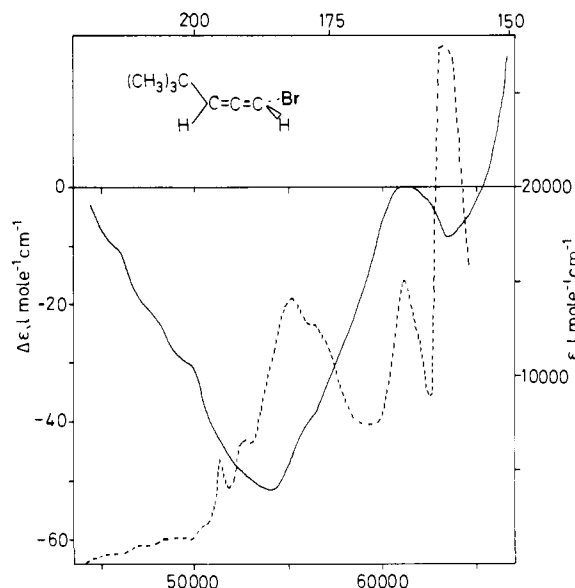


Figure 11. Gas-phase vacuum-UV absorption (---) and CD spectra (—) of 1-bromo-4,4-dimethyl-1,2-pentadiene (**3**).

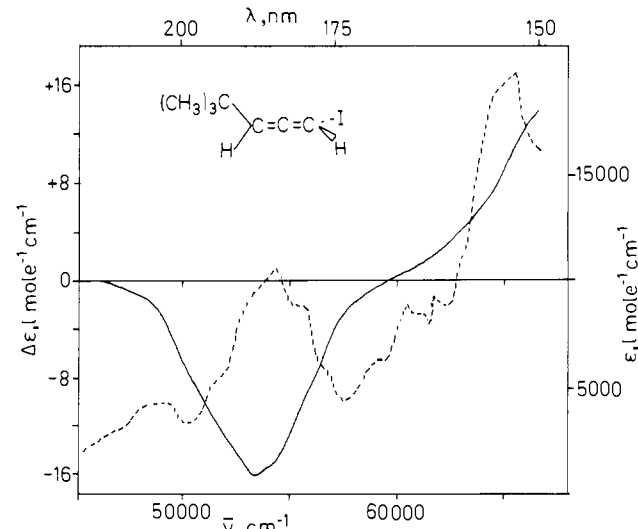


Figure 12. Gas-phase vacuum-UV absorption (---) and CD spectra (—) of 1-iodo-4,4-dimethyl-1,2-pentadiene (**4**).

While at lower energies ($\bar{\nu} < 45\,000\text{ cm}^{-1}$) all the observed excitations are of intravalence character, at higher energies Rydberg transitions are expected to play a significant role for the absorption and CD spectra. The empirical assignments of (extravalence or) Rydberg transitions are based mainly on their fit to the Rydberg formula (eq 4) and the sharpness of the Rydberg bands. Fur-

$$h\nu = \Delta E = IP - R/(n - \delta)^2 = IP - T_n \quad (4)$$

thermore, Rydberg bands (observed in the gas phase) disappear (or suffer a marked blue shift) in condensed phases.^{34,35}

In eq 4 $h\nu$ is the energy of the Rydberg transition and IP the ionization potential to which the Rydberg series converges; i.e., the "term value" $T_n = R/(n - \delta)^2$ corresponds to the ionization energy of the corresponding Rydberg state. R is the Rydberg constant, n the principal quantum number, and δ is the so-called quantum defect with typical values for s-, p-, and d-type Rydberg orbitals. Usually, the first member of a Rydberg series agrees poorly with the frequency predicted by eq 4. However, the term value remains a characteristic feature for the identification of transitions terminating at 3s, 3p, and 3d Rydberg orbitals. For many organic chromophores the term values depend on the molecular size and reach a limit when the molecule contains six to eight carbon (or other heavy) atoms. Since the four investigated

Table III. Energies and Term Values of the Rydberg States of Allenes (CH₃)₃CCH=C=CHX

origin ^a	Rydberg orbital	1 (X = (CH ₃) ₃ C)		2 (X = Cl)		3 (X = Br)		4 (X = I)	
		$\bar{\nu}$, cm ⁻¹	T_n , cm ⁻¹	$\bar{\nu}$, cm ⁻¹	T_n , cm ⁻¹	$\bar{\nu}$, cm ⁻¹	T_n , cm ⁻¹	$\bar{\nu}$, cm ⁻¹	T_n , cm ⁻¹
$\pi_X(I_1)$	3s	49 510 ^c	21 230	52 630	22 380	51 280	22 120	49 260	21 560
$\pi_X(I_1)$	3p	51 610 ^c	19 120					51 810	19 010
$\pi_X(I_1)$	3d	57 140	13 590					56 820	14 000 ^c
$\pi_X(I_1)$	4s					61 070	12 330	59 170	11 650
$\pi_X(I_1)$	4p	62 020	8 720					62 890	7 920
$\bar{\pi}_{Alk}(I_2)$	3s	53 000 ^d	21 850	58 140	20 900	55 940	21 890		
$\bar{\pi}_{Alk}(I_2)$	3p							55 550	19 300
$\bar{\pi}_{Alk}(I_2)$	3d					62 990	14 840 ^b	60 610	14 240
$\pi_X(I_3)$	3s					62 990	21 940 ^b	56 820	22 550 ^c
$\pi_X(I_3)$	3p							61 160	18 210
$\pi_X(I_3)$	3d							65 570	13 790 ^d

^a For the allenic hydrocarbon **1** the orbitals correspond to $e_1(I_1)$ and $e_2(I_2)$ (Table I). ^b Alternative assignments, $n_{Br} \rightarrow 3s$ being more probable. ^c Alternative assignments. ^d Superimposed on the ($\bar{\pi}_{Alk}, \bar{\pi}^*_{Alk}$) valence-shell transition. ^e $^1E(e_1 \rightarrow 3s)$. ^f $^1A_2(2e \rightarrow 3pe)$ or $^1E(2e \rightarrow 3pb_2)$. ^g $^1E(e_2 \rightarrow 3s)$.

molecules contain at least seven carbon atoms the 3s, 3p, and 3d Rydberg states are expected to have energies of $\sim 22\,000$ cm⁻¹, $\sim 19\,000$ cm⁻¹, and $\sim 14\,000$ cm⁻¹, respectively, below the first ionization potential. For tetramethylallene (**13**), for instance, a term value of $20\,700$ cm⁻¹ has been observed for the 3s Rydberg excitation.¹¹ The same pattern should be exhibited for Rydberg excitations converging to higher ionization potentials. Since in the four investigated Allenes the splitting between the first two ionization potentials is only ca. 0.5 eV, Rydberg excitations converging to the second IP can be observed at wavenumbers $\bar{\nu} < 66\,000$ cm⁻¹. Furthermore, owing to the low ionization energies of the n_{Br} and n_I (lone-pair) orbitals, the bromo and iodo compounds **3** and **4** are expected to have $n_{Br} \rightarrow 3s$ and $n_I \rightarrow 3s$ and $n_I \rightarrow 3p$ Rydberg states with energies less than $66\,000$ cm⁻¹.^{40b}

Referring to the above discussion, an interesting consequence for the Allenes **1** and **4** emerges. Compounds **1** and **4** should exhibit corresponding Rydberg states at almost the same energies, as **1** and **4** have the same values for their ionization potentials. In **1** the two expected Rydberg series converge to the ionization potentials (e_1 and e_2 ; Table I) of the pseudo-Jahn-Teller components of the (quasi) 2E state of the molecular ion 1^+ .

In an allenic chromophore of symmetry D_{2d} (in particular, in the parent molecule **5**) allowed Rydberg states derived from group-theoretical arguments are $E(e \rightarrow ns)$, B_2 and $E(e \rightarrow np)$, and B_2 and $E(e \rightarrow nd)$. All the other Rydberg transitions are electrically forbidden. We therefore expect for Allenes with a lower symmetry all the Rydberg series to show up. As it happens with many substituted chromophores some Rydberg transitions are missing. We attribute their nonappearance to the general mechanisms used to explain broadening of the spectral bands at high energies, i.e., predissociation or internal conversion to lower Rydbergs or Rydbergs of other symmetries.

As was pointed out, the PE spectra of the four Allenes **1-4** do not show the rich vibrational structure observed for allene (**5**). This is reflected also in the vacuum-UV absorption spectra where only the 3s Rydberg excitation of the bromoallene **3** (Figure 11) exhibits a clear vibrational progression. This progression in **3** consists of three bands separated by 1130 ± 30 cm⁻¹. It may be tentatively associated with the b mode of the =C—H bips (E) (section III.2) which is also observed for the lowest excited state ($S_1(^1A_2)$) of **1**. The progression, however, may also correspond to the symmetric C=C=C stretch which is found in PE band 1 of **3**. The proposed assignments of the various Rydberg transitions in the four Allenes **1-4** are presented in Table III.

These assignments require some additional remarks. In 1,3-di-*tert*-butylallene (**1**) (Figure 9) a shoulder at $53\,000$ cm⁻¹ in absorption may be a vibrational component of the strong $54\,420$ -cm⁻¹ band. This last strong band corresponds to the 1B_2 excited state which results from the only electric dipole allowed transition associated with the $2e \rightarrow 3e$ excitation of D_{2d} allene

(**5**).⁷⁻⁹ According to quantum-chemical calculations,^{7a} the 1B_2 band of **5** corresponds rather to a state of "mixed" character than one resulting from a pure intravalence transition. The diffuseness of this band indicates that the state is more of intravalence than Rydberg character.

The $53\,000$ cm⁻¹ shoulder of the 1B_2 band of **1** cannot be observed in the CD. This indicates that the shoulder does not have the electronic characteristics of the 1B_2 band. Tentatively, it is assumed that it corresponds to a separate band with pure Rydberg character. In particular, it is attributed to the second component ($e_2 \rightarrow 3s$) which results from the 2E state of the ionic core of **1**. Such a split of the lowest member of the 3s Rydberg series, $^1E(e \rightarrow 3s)$, has also been suggested for allene (**5**) by Robin³⁴ and Fuke and Schnepf.⁹

A Rydberg $e_1 \rightarrow 3p$ state of **1** can only be observed in CD as a very sharp peak at $51\,600$ cm⁻¹. It is an open question whether this peak (with a negative CD) corresponds to $e_1 \rightarrow 3p$ or whether it has a positive CD so that the sharp inlet at $51\,950$ cm⁻¹ is to be associated with $e_1 \rightarrow 3p$. Finally, the CD band shape can also be generated by an oppositely signed CD couplet. The absence of a corresponding absorption band can be explained as a strongly magnetically allowed transition. Hence, the sharp negative CD band at $51\,600$ cm⁻¹ can be assigned to a $^1A_2(e_1 \rightarrow 3p)$ Rydberg transition which is magnetic dipole allowed and electric dipole forbidden. This $^1A_2(3p)$ Rydberg is one of the four Rydberg states resulting from the e (valence-shell) $\rightarrow 3pe$ (Rydberg) excitation. Alternatively, the last CD band (or CD couplet, respectively) can also be explained as a $^1E(e \rightarrow 3pb_2)$ Rydberg state where the corresponding excitation has also a considerable magnetic transition moment.^{7a} For allene (**5**) both these last Rydberg states are calculated to have very close energies.⁷

The valence-like states of the halogenoallenes **2-4** correlating with 1B_2 in **1** are observed at almost the same energy positions. They are best described as (π_X, π^*_X) excitations with small admixtures from the ($\bar{\pi}_{Alk}, \bar{\pi}^*_{Alk}$) transitions.^{3b} For brevity these states will be termed (π_X, π^*_X). The energies of the (π_X, π^*_X) states (generating the first vacuum-UV absorption maxima) follow the π_X ionization energies of **2-4** (i.e., for $\bar{\nu}_{max}(\pi_X, \pi^*_X)$ one has the sequence $Cl > Br > I$ and $\bar{\nu}_{max}(\pi_1, \pi^*_1)$ of **4** being identical with $\bar{\nu}_{max}(^1B_2)$ of **1**).

The vacuum-UV spectrum of the chloroallene **2** (Figure 10) is extremely simple and exhibits only one broad intense band (resulting from (π_{Cl}, π^*_{Cl})). This band has a shoulder toward the blue region which is attributed to the $\bar{\pi}_{Alk} \rightarrow 3s$ Rydberg state (Table III).

The bromoallene **3** shows a vacuum-UV absorption spectrum with three intense bands and two medium, low-energy sharp bands. Equation 4 offers two alternative Rydberg assignments for the most intense sharp band at $62\,990$ cm⁻¹. It can originate with a $\bar{\pi}_{Alk} \rightarrow 3d$ excitation or with $n_{Br} \rightarrow 3s$, i.e., a Rydberg transition originating with the bromine lone pair. Of course, this last band can comprise both these Rydberg states. On the basis of the analogy with vinylbromide (**7b**) where $n_{Br} \rightarrow 3s$ is the most intense Rydberg absorption band (with the energy $\bar{\nu} = 62\,759$ cm⁻¹)^{44a}

(40) (a) Schander, J.; Russell, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 6900. (b) For the discussion of the enumeration of the first member of Rydberg series of molecules with Cl, Br, and I, cf. ref 40a.

Table IV. Excited States of Allenes (CH₃)₃CCH=C=CHX Resulting from Valence-Shell Excitations and Their Energies

state ^a	configuration	$\bar{\nu}$, cm ⁻¹		state ^b	configuration	$\bar{\nu}$, cm ⁻¹			
		1	2			3	4		
¹ A ₂	(1/2) ^{-1/2} ((π _z ,π* _y) - (π _y ,π* _z))	37 900		¹ A''	(π _X ,π* _{Alk}) - λ(π̄ _{Alk} ,π* _X)	38 170	36 400	37 410	
¹ B ₁	(1/2) ^{-1/2} ((π _z ,π* _y) + (π _y ,π* _z))	46 300		² A'	(π̄ _{Alk} ,π* _X) + λ(π _X ,π* _{Alk})	40 780	41 000	40 160	
				³ A'	(π _X ,σ* _{C-X})	48 540	45 660	42 920	
				¹ A'	(n _X ,σ* _{C-X})	51 020	49 650	48 950	
¹ B ₂	(1/2) ^{-1/2} ((π _z ,π* _z) - (π _y ,π* _y))	54 420		² A'	(π _X ,π* _X) - (π̄ _{Alk} ,π* _{Alk})	57 470	55 170	54 370	
¹ A ₁	(1/2) ^{-1/2} ((π _z ,π* _z) + (π _y ,π* _y))	≥65 000		³ A'	(π̄ _{Alk} ,π* _{Alk}) + (π _X ,π* _X)	≥65 000	≥65 000	65 570	

^aCorrelation with D_{2d} allene (5). ^bCorrelations with C_s Allenes (6a-8a).

we attribute the 62990-cm⁻¹ band in **3** primarily to the n_{Br} → 3s excitation without excluding that the n_{Br} → 3s band buries that of π̄_{Alk} → 3d.

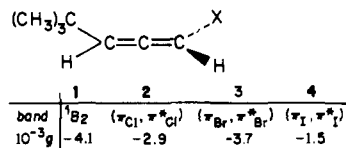
The absorption spectrum of the iodoallene **4** (Figure 12) is the most structured one. If alternative assignments for the shoulder at 56820 cm⁻¹ are accepted, all the Rydberg states originating with the three highest energy orbitals π_I, π̄_{Alk}, and n_I and terminating at the 3s, 3p, and 3d Rydberg orbitals are observed (only π̄_{Alk} → 3s cannot be found).

The gas-phase CD spectra of the Allenes **1-4** over the spectral range 40000-66000 cm⁻¹ show almost the same pattern. A broad positive featureless band is found at 40820 cm⁻¹ for the chloro compound **2** (Figure 10) and at 45460 cm⁻¹ for the C₂ dialkylallene **1** (Figure 9). Due to the low vapor pressure, corresponding bands were not detected for **3** and **4**. The weak CD bands are followed by strong negative bands with maxima near 55000 cm⁻¹. Toward the red region the strong negative CD bands have shoulders of the same signs. As has been discussed the CD spectrum of **1** reveals an additional sharp negative CD band at 51600 cm⁻¹ which does not have a corresponding absorption band (Table III).

The strong negative CD bands are associated with the intense absorption bands at the same positions and, hence, correspond to the ¹B₂ state of **1** and (π_X,π*_X) states of **2-4**, respectively. The high-energy positive CD bands ($\bar{\nu} \geq 65000$ cm⁻¹) can be assigned to the valence-like ¹A₁(e → e) excited state of **1** (which is electric dipole forbidden in the D_{2d} allenic chromophore) and the (π̄_{Alk},π*_{Alk}) excited states of **2-4**, respectively. For **4** this excited state is found at ca. 65000 cm⁻¹ (Table III, ref d). The (π̄_{Alk},π*_{Alk}) transitions of **2-4** are electrically allowed by symmetry but should remain weak due to small transition moments.^{5a} In Table IV a summary of the (low- and high-energy) intravalence excited states of the Allenes **1-4** is given together with the corresponding electronic configurations. The assignments of the two highest energy excited states of **1-4** can rely on dynamic coupling theory³³ which, for (R)-1,3-dialkylallenes such as **1** or **10**, predicts a positive rotatory strength for ¹A₁ (see previous section III.2) and a negative one for ¹B₂. Similarly, as the CD bands of the (π_X,π*_X) transitions in **2-4** correspond in shape largely to those of the ordinary absorption bands, it is reasonable to conclude that the electronic transitions (and their vibrational components) responsible for the electric dipole strengths are largely responsible for the rotatory strengths as well. This means that the optical activity of the strong 55000-cm⁻¹ CD bands of (R)-Allenes **2-4** can be rationalized in terms of a dipole-dipole coupling of the electrically allowed (π_X,π*_X) and (π̄_{Alk},π*_{Alk}) transitions, similarly to the situation discussed for phenylallene-carboxylic acid (C₆H₅CH=C=CHCOOH).^{3a,14} Such a mechanism gives a negative sign for the states (π_X,π*_X) - (π̄_{Alk},π*_{Alk}) and a positive one for (π̄_{Alk},π*_{Alk}) + (π_X,π*_X) (neglecting the coefficients, cf. ref 41) for Allenes with R configurations.

The split of 11000-13000 cm⁻¹ between ¹B₂ and ¹A₁ or (π_X,π*_X) and (π̄_{Alk},π*_{Alk}), respectively, resulting from our assignment in Table III corresponds to that calculated for allene (**5**) by Rauk^{7a} ($\bar{\nu}(\sup{1}A_1) - \bar{\nu}(\sup{1}B_2) = 10650$ cm⁻¹). A somewhat larger split is calculated for chloroallene **6a** (15580 cm⁻¹).^{5a,41}

If one compares electronic features of **1-4** by the dissymmetry ratio $g = 4R/D \approx \Delta\epsilon/\epsilon^{42}$ of the ¹B₂ and (π_X,π*_X) bands, respectively, it is to be noted that **1-3** have almost the same g values ($g \approx (3-4) \times 10^{-3}$), which are similar to those found for the (π,π*) bands of chiral cyclic ethylenes.^{15,16a} Iodoallene **4**, however, has a g value which is ca. one-half of those observed for **1-3**. We



regard this as a support of our deduction that the electronic features of the chloro- and bromoallene **2** and **3** are similar to that of **1** (π_X and π*_X retaining largely their allenic characters), whereas in the iodoallene **4** the orbitals (in particular, π_I) are subjected to larger (conjugative) perturbations.

Finally, it is to be noted that the gas-phase spectra of the optically active Allenes **1-4** are dominated by valence-type transitions. Almost no CD signals are assigned to Rydberg excitations. This is surprising if, in particular, the CD features of the allene chromophore (in **1**) are compared with those of the structurally related ethylene chromophore,^{15,16} where π → 3s and π → 3p Rydbergs are the transitions having the largest dissymmetry factors g . One should be aware, however, that both chromophores differ essentially by the natures of their lowest excited (singlet) states. In the ethylene chromophore mostly the 3s Rydberg state is the one of lowest energy.^{15,16,35}

On the other hand, in the allene chromophore the Rydberg 3s state is preceded by two valence-shell transitions, i.e., the discrete-type 3s Rydberg excitation is embedded into a continuous or highly dense vibrational manifold of electronic excitations of quite different origins, namely ¹B₁ toward the red region and ¹B₂ toward the blue region. Therefore, either the CD of the 3s Rydberg is decreased simply by overlap with the ¹B₁ CD band of opposite sign (as has been proposed for the reduction of intensity of the ¹B₁ CD band going from the condensed phase to the gas phase in III.2) or an interference effect is operative, as is discussed for chiral C₂ molecules by Hansen and Bouman.⁴³ Similarly, for the halogenoallenes **2-4** the Rydberg π_X → 3s is embedded in three valence-shell transitions, namely (π_X,σ*_{C-X}), (n_X,σ*_{C-X}), and (π_X,π*_X).

The empirically found data in Tables III and IV for **1** with the allene chromophore provide good evidence for the sequence and the natures of the excited states of allene (**5**). In this regard our results correspond in many aspects to the results of the vertical excitation energy (ab initio) calculation for **5** by Rauk.^{7a} They are, however, considerably at variance with Segal's calculations.^{7b}

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(41) In ref 5a only results for the ¹A'(π_{Cl},π*_{Cl}) state are given for **6a**: $\Delta E(0.78(\pi_{Cl},\pi^*_{Cl}) - 0.58(\bar{\pi},\bar{\pi}^*)) = 51900$ cm⁻¹. The same calculations give $\Delta E(0.77(\bar{\pi},\bar{\pi}^*) + 0.53(\pi_{Cl},\pi^*_{Cl})) = 67480$ cm⁻¹.

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