The Molecular Structure of Allenes and Ketenes. Part 20.[1] Excited States of 3-Halogeno- and Other 3-Substituted Phenylallenes: Circular Dichroism and Absorption Spectra, and CNDO/S Calculations

Harold F. Baumann *
Laboratory for Organic Chemistry, Federal Institute of Technology, CH-8092, Zürich, Switzerland
Cornelis J. Elsevier and Peter Vermeer
Department of Organic Chemistry, State University, 3584 CH Utrecht, The Netherlands
Wolfgang Runge *,†
Institut für Struktur- und System-forschung, D-6900 Heidelberg, W. Germany

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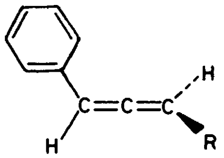
Excited states of phenylallenes $C_6H_5CH{=}C{=}CHR$ with energies $\tilde{\nu} \leqslant 52\,000$ cm^{-1} have been investigated by means of circular dichroism [R = Cl (**4**), R = Br (**5**), and R = I (**6**)] and u.v. absorption spectroscopy [R = MeO (**1**), R = CO$_2$H (**2**), R = CN (**3**), and (**4**)—(**6**)]. Semiempirical CNDO/S-CI calculations including singly and doubly excited configurations for (**1**)—(**4**) have been used to support and specify the empirical inferences about excited states. Furthermore, the theoretical results have provided band assignments for certain electronic bands of phenylallenes with acceptor groups [(**2**) and (**3**)]. Substituent effects on the lowest-energy intense absorption bands [excited state $S_4(\pi,\pi^*)$] are discussed in more detail for a series of phenylallenes [(**1**)—(**6**) and R = H (**7**), R = Me (**8**), and R = Bu^t (**9**)]. It is suggested that in producing the marked shift of the $S_4(\pi,\pi^*)$ band of the 3-halogeno-1-phenylallenes (**4**)—(**6**) relative to (**7**), hyperconjugation across the allenic C=C=C system plays an important role.

In this contribution low-energy excited singlet states of the phenylallenes (**1**)—(**6**) with $\tilde{\nu} \leqslant 52\,000$ cm^{-1} are investigated, and substituent effects on the particular excited state $S_4(\pi,\pi^*)$ for the series (**1**)—(**9**) are studied.

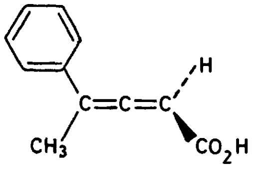


	(1)	(2)	(3)	(4)	(5)
R =	OMe	CO$_2$H	CN	Cl	Br
	(6)	(7)	(8)	(9)	
R =	I	H	Me	Bu^t	

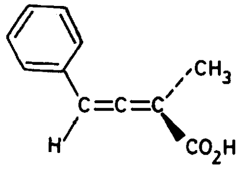
Previous investigations of the phenylallene chromophore [represented by (**7**) and the homologues (**8**) and (**9**)] have revealed that, in terms of configuration interaction (CI), descriptions and theoretical calculations of several excited states require the inclusion of doubly excited (DE) electronic configurations.[2] It therefore seemed of interest to extend knowledge of the role of DE configurations for excited states to various other 3-substituted phenylallenes.

For these purposes u.v. absorption spectra of (**1**)—(**6**) and circular dichroism (c.d.) spectra of (**4**)—(**6**) [of known (*S*)-(+) absolute configuration][3] were measured. In order to corroborate empirical inferences and assign certain electronic bands, semiempirical CNDO/S-CI calculations including singly and doubly excited (SE and DE) configurations were performed for (**1**)—(**4**). We expected that the CNDO/S calculations, furthermore, would aid in 'resolving' experimentally observed spectral bands, if they predicted more excited states than are found experimentally.

The u.v. absorption spectrum of (**2**) and the u.v. and c.d. spectra of related phenylallenecarboxylic acids, such as (**10**) and (**11**), are discussed in ref. 4.



(**10**)



(**11**)

In the light of the results for the phenylallene hydrocarbons (**7**)—(**9**),[2] the assignments of the electronic bands of (**2**), (**10**), and (**11**) suggested in ref. 4 are partly revised in this paper, utilizing CNDO/S-(SE + DE)-CI calculations for (**2**).

Among the low-energy excited states of phenylallenes, $S_4(\pi,\pi^*)$[2,4] plays a key role in relation to a basic concept of allene chemistry. For more than 30 years a fundamental approach to discussions of chemical and physical properties of allenes has rested on the assumption that either double bond of the C=C=C grouping may be considered comparable to an insulated ethylenic bond in its availability for resonance with other groups attached to it.[5] Hence, properties of a complex allene $R^1R^2C{=}C{=}CR^3R^4$ are considered as related to those of two isolated constituent ethylenic subunits $R^1R^2C{=}CH_2$ and $H_2C{=}CR^3R^4$. For excited states and u.v. absorption spectra, in particular, two isolated chromophores are assumed to exist in allenes.[5]

Recently, numerous objections to this simple model have been raised.[1,2,6–9] One of the most striking examples of the inadequacy of the model is provided by the u.v. absorption spectra of the 3-halogeno-1-phenylallenes (**4**)—(**6**), which exhibit a marked bathochromic shift with respect to the phenylallene (**7**) S_4 band ($\tilde{\nu}$ = 40 400 cm^{-1}):[2] $\tilde{\nu}(4)$ = 39 030, $\tilde{\nu}(5)$ = 37 650, $\tilde{\nu}(6)$ = 34 800 cm^{-1}; *cf.* Table 2. According to the simple model the S_4 position should be (almost) independent of the 3-substituent. Absorption data have been given previously in the literature for (**5**)[10] and (**6**);[11] however, no comment was made on the substituent effect. On the other hand, a corresponding u.v. band shift has also been found for 1,1-diphenyl-3-halogenoallenes (**12**)—(**14**), and attributed to 'hyperconjugative interactions between the 1,1-diphenylstyrene subunit and the halogen atoms.'[12] Hyperconjugative interac-

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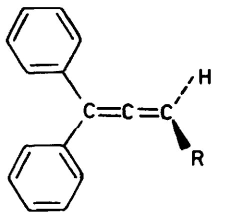
† *Present address:* Dow Chemical Rheinwerk, D-7587 Rheinmuenster, W. Germany.



(12)	(13)	(14)
R = Cl	Br	I

tions between the phenyl and the remote groups R were indeed observed in the ^{13}C n.m.r. chemical shifts of (**1**)—(**8**).[9] Here, two types of interactions, π-type CHR hyperconjugation and $\bar{\pi}$-type CHPh hyperconjugation, were differentiated.

A statement about the operation of hyperconjugative interactions, however, is too general to be of value to explain the substituent effect on the S_4 band position. For 3-alkyl-1-phenylallenes [$\tilde{\nu}$(**8**) = 39 900, $\tilde{\nu}$(**9**) = 39 680 cm^{-1}][2] and the phenylallenecarboxylic acid (**2**) ($\tilde{\nu}$ = 40 500 cm^{-1})[4] the S_4 shifts are not dramatic; therefore the question arises as to whether or not significant S_4 band shifts are restricted to the halogen substituents and, in particular, whether or not they are due to the halogen *d* atomic orbitals. The effect might be related to the special electronic situation of the atoms Cl, Br, and I, with perpendicular *p* orbitals (p_y, p_z). This last proposition may be assessed by study of the substituent effect of the cyano group (a pseudohalide) on S_4. Furthermore, the investigation of the cyanoallene (**3**) was expected to cast light on the question as to whether the strong π-acceptor character of the substituent has a direct influence on S_4. The medium-strength acceptor CO_2H generates only a small hypsochromic shift of S_4. Finally, the investigation of the methoxy compound (**1**) (strong π-donor MeO) was expected to show how far the S_4 band is affected by the substituent's donor character.

Experimental and Computational

Syntheses of the racemic allenes (**1**)—(**6**) are described in refs. 3 and 9. Optically pure (**4**)—(**6**) of (*S*)-(+) configuration were prepared according to the method given in ref. 3.

The u.v. absorption spectra of the allenes (**1**) and (**3**)—(**6**) were run with a PMQ II Zeiss spectrophotometer or a Perkin-Elmer 555 u.v.–visible spectrometer for solutions in iso-octane, n-hexane, and acetonitrile solutions (spectral resolution at 40 000 cm^{-1} was *ca.* 50 cm^{-1}). The c.d. spectra of (**4**)—(**6**) were measured with a Jouan c.d. dichrograph for solutions in n-hexane (spectral resolution at 40 000 cm^{-1} was *ca.* 40 cm^{-1}). Low-temperature c.d. spectra of (**6**) were measured for solutions in methylcyclohexane–isopentane (1:3). C.d. experiments were performed with samples having optical purities of *ca.* 40%. The measured c.d. data were converted to values for compounds of 100% optical purity.[3]

Semiempirical vertical excitation energy ($\Delta\tilde{E}$) and oscillator strength ($\tilde{f}$) CNDO/S-(SE + DE)-CI calculations (with use of standard geometries for the allenic skeleton and the substituents) were carried out as described recently.[2]

Results and Discussion

Phenylallenes with a First-row Substituent.—Absorption spectra of (**1**) and (**3**) are displayed in Figure 1. In the following discussion, as usual,[2,4,7–9] orbitals of (**1**)—(**6**) and (**8**) and (**9**) correlating with a″ orbitals of phenylallene (**7**) will be denoted by π, and those correlating with the outermost a′ MOs of (**7**) by $\bar{\pi}$. Excited states will be characterized in terms of excitations localized at the allenic or benzene moiety, respectively.[2,4]

3-*Methoxy*-1-*phenylallene*. Except for the longest-wavelength region the methoxy compound (**1**) exhibits an absorption spectrum very close to that of 3-methyl-1-phenylallene (**8**).[2] Both (**1**) and (**8**) have donor substituents, and hence the general electronic features involving the π orbitals should be similar. Based on the results for (**8**),[2] the band assignments for (**1**) are straightforward and are summarized in Table 1. Though the methoxy group is a considerably stronger donor than the methyl group the S_4 band maxima of (**1**) and (**8**) are at almost the same positions. Therefore, the energetic position of S_4 seems not to be influenced significantly by the donor character of the 3-substituent.

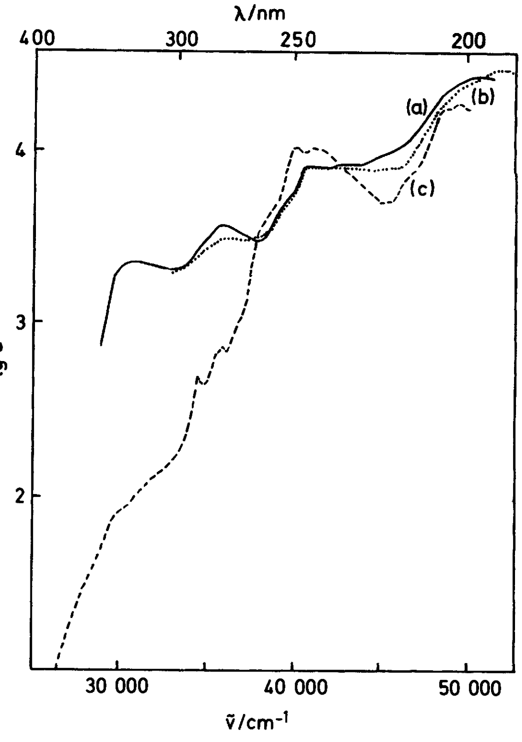


Figure 1. U.v. absorption spectra of 3-cyano-1-phenylallene (**3**) (a) in CH_3CN, (b) in n-hexane, and (c) 3-methoxy-1-phenylallene (**1**) in n-hexane

Recently, it has been revealed that the strong S_4 band of (**7**)—(**9**) is generated by a further state, $S_5(E_{2g})$, which results mainly from $[\pi_{(1)},\pi_{(3)}{}^*]$ excitation, but contains large contributions from the HOMO ⟶ LUMO $[\pi_{(1)}\pi_{(1)}{}^*,\pi_{(1)},\pi_{(1)}{}^*]$ double excitation.[2] The u.v. spectrum of (**1**) exhibits a shoulder at 39 400 cm^{-1}, *i.e.* 700 cm^{-1} to the red from the strong S_4 band. This shoulder is associated with $S_5(E_{2g})$ (Table 1).

The suggested band assignments for (**1**) are supported by CNDO/S-(SE + DE)-CI calculations (Table 1). In particular, the corrected energies given in parentheses show good agreements with the experimental values. The calculations predict the existences of two further excited states (S_7, S_9) which cannot be detected in the absorption spectrum. Both result from excitations with very low transition probabilities. Hence, they will be buried by the strong bands. The theoretical results for (**1**) are almost identical with those for (**8**).[2] In particular, they have the same sequence of excited states S_1—S_{10} (with almost the same energies $\Delta\tilde{E}$ and oscillator strengths $\tilde{f}$). Furthermore, for (**1**) and (**8**) the CI compositions of the excited states are nearly identical.

In ref. 2 it has been shown that S_5 has a distorted geometry, *i.e.* the vertical excitation energy calculation cannot reproduce its energy. For (**8**) the theoretical vertical excitation energy of S_5 is too high by 1.56 eV relative to the experimental value. Almost the same difference is observed for (**1**) (1.63 eV; Table 1).

3-*Cyano*-1-*phenylallene*. The u.v. absorption spectrum of the cyano compound (**3**) differs in several aspects from the u.v. spectra of all the other phenylallenes with a first-row substituent in the 3-position.[2,4,13] There is not even a similarity to the spectra of phenylallenecarboxylic acids, such as (**2**),[4] which also bears an acceptor group. The most apparent difference between **(3)** and **(1)**, **(2)**, and **(7)**—**(9)** is its high polarity (calculated dipole moment, $\mu = 4.65$ D) and the availability of two $\bar{\pi}_{(i)}$ [$\bar{\pi}_{(i)}^*$] orbitals within the manifold of $\pi_{(i)}$ [$\pi_{(1)}^*$] MOs. In a composite-molecule approach the $\bar{\pi}_{(i)}$ [$\bar{\pi}_{(i)}^*$] orbitals result from interactions of the phenylallene $\bar{\pi}_A(a')$ orbitals with the corresponding $\bar{\pi}_{CN}$ orbitals of the cyano group [for instance, $\bar{\pi}_{(1,2)} = N_\pm\ (\bar{\pi}_A \pm \lambda_\pm\ \bar{\pi}_{CN})$]. These last CN orbitals correlate with the corresponding $\pi_{(i)}$ orbitals of cyanoallene ($H_2C{=}C{=}CHCN$).[14]

The band assignments for **(3)** together with the theoretical results are given in Table 1 and require some comments. Apart from $S_3(B_{2u})$ with $\varepsilon \approx 500$—1 000 (as in other phenylallenes), the 35 840 cm^{-1} band of **(3)** is generated by at least one further excited state. The corresponding band (with $\varepsilon \approx 2\,000$) should result from a transition with a medium-strength electric transition moment.

The foregoing suggestion is supported by the observation of a considerable reduction of the intensity of the 35 840 cm^{-1} band on changing the polar solvent acetonitrile to the non-polar n-hexane (Figure 1). The $S_3(B_{2u})$ band in isolation neither changes its position nor its intensity significantly in other phenylallenes, if a polar solvent (ethanol) is substituted by a non-polar one (n-hexane).[2,4,13] Furthermore, we take the sensitivity of the intensity of the 35 840 cm^{-1} band towards changes of solvent as an indication of the polar nature of the second excited state of that band. According to the CNDO/S calculations an electrically weakly allowed excitation, $S_5[\bar{\pi}_{(1)},\bar{\pi}_{(2)}^*]$, should be found near 36 000 cm^{-1}. This state involves the orbitals $\bar{\pi}_{(1)} \approx (\bar{\pi}_A - \bar{\pi}_{CN})$ and $\bar{\pi}_{(2)}^* \approx (\bar{\pi}_{CN}^* - \bar{\pi}_A^*)$ which are localized essentially at the allenic or CN sites, respectively. Therefore, the band $S_5[\bar{\pi}_{(1)},\bar{\pi}_{(2)}^*]$ has considerable charge-transfer (c.t.) character and, in this way, is in agreement with the observed polarity of the 35 840 cm^{-1} state. It is an open question, however, whether a further c.t. state, $S_6[\bar{\pi}_{(2)},\bar{\pi}_{(1)}^*]$, calculated to lie 0.67 eV to the blue of S_5 (Table 1), contributes also to the 35 840 cm^{-1} band or is buried by the strong u.v. bands at higher energies.

After the rise to the u.v. band maximum at 40 800 cm^{-1} which is associated with $S_4(B_{1u})$ the absorption intensity of **(3)** does not decrease; instead of a separate S_4 band a plateau appears (Figure 1). Comparisons of the u.v. spectra of **(3)** in acetonitrile and n-hexane suggest that the plateau contains at least two electronic bands, at 42 600 and *ca.* 45 000 cm^{-1}. Relative to acetonitrile the absorption intensity is reduced in n-hexane and the small hump at 42 600 cm^{-1} as well as the shoulder near 45 000 cm^{-1} disappear. The phenylallene hydrocarbons **(8)** and **(9)** have a magnetically allowed, electrically forbidden (m.a., e.f.) transition $[\bar{\pi}_{(1)},\pi_{(2)}^*]$ at 43 000 cm^{-1},[2] and also for **(1)** a corresponding transition is assigned to the 43 000 cm^{-1} u.v. shoulder (S_6; Table 1). This transition has considerable c.t. character and, hence, could explain the observed solvent sensitivity of the 42 600 cm^{-1} band of **(3)**. The theoretical calculations, however, attribute a different m.a., e.f. transition with a large c.t. character to the 42 600 cm^{-1} band, namely $[\pi_{(2)},\bar{\pi}_{(1)}^*]$. The corresponding state, S_9 (Table 1), has considerable contributions from DE configurations. The former state, $S_{11}[\bar{\pi}_{(1)},\pi_{(2)}^*]$, is calculated to be only 0.12—0.15 eV to the blue of $S_9[\pi_{(2)},\bar{\pi}_{(1)}^*]$. Hence, both these c.t. states would explain the observed solvent effects on the 42 600 and 45 000 cm^{-1} bands.

For energetic reasons the cyanoallene **(3)**, like all the other phenylallenes, should have its electrically allowed $E_{1u(a)}$ state near 45 000 cm^{-1}.[2,4,14] For **(3)**, however, the corresponding band is not separated from the subsequent band, as for **(1)** (Figure 1). The existence of that state (S_8) is supported by the CNDO/S results.

The highest-energy broad band with a maximum at 50 670 cm^{-1} (in acetonitrile) should contain two electrically allowed states, $E_{1u(b)}$ and $[\bar{\pi}_{(1)},\bar{\pi}_{(1)}^*]$, localized at the benzene or allene moiety, respectively.[2,4] $[\bar{\pi}_{(1)},\bar{\pi}_{(1)}^*]$ of **(3)** correlates with the HOMO ⟶ LUMO (π,π^*) excitation in $H_2C{=}C{=}CHCN$.[14] According to the CNDO/S calculations (S_{10}, S_{12}; Table 1), $E_{1u(b)}$ and $[\bar{\pi}_{(1)},\bar{\pi}_{(1)}^*]$ of **(3)** are mixed considerably.

Phenylallenecarboxylic acids. With the CNDO/S-(SE + DE)-CI scheme it is now possible to understand the u.v. and c.d. spectra of phenylallenecarboxylic acids [**(2)**, **(10)**, and **(11)**][4] much better (Table 1). In the low-energy part ($S_1 - S_4$) the calculations reverse the sequence of the lowest-energy excited states. According to empirical evidence, however, the lowest-energy excited state should involve the $[\bar{\pi}_{(1)},\pi_{(1)}^*]$ configuration (28, 31) as the leading term in the CI expansions.[4]

The c.d. bands of the phenylallenecarboxylic acids are heavily structured in the region $38\,500 \leqslant \tilde{\nu} \leqslant 44\,000$ cm^{-1}.[4] It has been assumed that much of this structure is due to vibrational bands. However, the strong variations of the g values ($\Delta\varepsilon/\varepsilon$) in this range (Figure 7 in ref. 4) indicate that at least three excited states contribute to this region with energies $\tilde{\nu} \approx 39\,000$ (S_6), $\tilde{\nu} \approx 40\,500$ cm^{-1} (S_4), and $\tilde{\nu} \approx 43\,000$ cm^{-1} (S_8). In the absorption spectrum of **(2)** only one maximum is seen, at 40 500 cm^{-1}; this is also found at 40 500 cm^{-1} for **(11)**.[4] For energetic reasons the 39 000 cm^{-1} band is attributed to the state S_6 with a significant contribution from the ($\pi\pi^*,\pi\pi^*$) DE configuration. According to the CNDO/S results the strong 40 500 cm^{-1} absorption band should comprise a further state, $S_5(n,\bar{\pi}^*)$, which cannot be detected experimentally. The existence of such a state at that position is reasonable, as alkylallenecarboxylic acids have their (n,π^*) excitations around 40 000 cm^{-1}.[7] Furthermore, for **(2)** a band near 40 000 cm^{-1} in addition to those found for **(1)** and **(3)** is suggested by the absorption intensity. For **(2)** one finds $\varepsilon = 17\,450$ for the 40 000 cm^{-1} u.v. band,[4] whereas for **(1)** and **(3)** the corresponding bands only have half that intensity (Table 1).

The 43 000 cm^{-1} bands of the phenylallenecarboxylic acids have the largest g values (2—4 $\times$ 10^{-3}).[4] This indicates that the corresponding excited state has a large magnetic moment. According to the CNDO/S calculations the 43 000 cm^{-1} band should correspond to the $S_8[\pi_{(2)},\bar{\pi}_{(1)}^*]$ state. It cannot be ruled out, however, that a further m.a., e.f. transition, $S_{10}[\bar{\pi}_{(1)},\pi_{(2)}^*]$, contributes to that spectral range (Table 1).

For the high-energy absorption band [$\tilde{\nu}_{max.} = 48\,800$ cm^{-1} for **(2)**] low-temperature absorption spectra reveal two additional bands at 46 000 and 47 000 cm^{-1}.[4] The intensities of these last bands are reversed on changing ethanol as solvent to a hydrocarbon (Figure 6 in ref. 4). This solvent effect indicates that the bands are due to two different electronic states and not to vibrational components of one electronic band. This is supported by the fact that for the 46 000 cm^{-1} absorption band a corresponding c.d. band is found, whereas for the 47 00 cm^{-1} band the c.d. changes its sign.[4] Hence, the high-energy strong absorption band of **(2)** comprises at least three electronic states. The calculations predict four excited states (S_9 and S_{11}—S_{13}) to exist in that energetic region. All these states have complex CI-compositions and can be interpreted approximately as mixing of the $E_{1u(b)}$ and $[\bar{\pi}_{(1)},\bar{\pi}_{(1)}^*]$ states. On the other hand, the $E_{1u(a)}$ state (S_7) remains largely pure (Table 1).

Summary. The essential excited state characteristics of phenylallenes with first-row substituents in the 3-position are summarized in Table 2. The role of DE configurations for the descriptions of these states is given in the seventh column.

For the phenylallenes **(1)**—**(3)** and **(7)**—**(9)** the excited state of special interest, S_4, near 40 000 cm^{-1}, has no significant contributions from DE configurations; S_4 involves essentially the $[\pi_{(1)},\pi_{(1)}^*]$ and $[\bar{\pi}_{(1)},\bar{\pi}_{(1)}^*]$ configurations and can be described approximately according to equation (1). For the

$$S_4(B_{1u} + B_2) \approx 0.9\ [\pi_{(1)},\pi_{(1)}^*] - 0.4\ [\bar{\pi}_{(1)},\bar{\pi}_{(1)}^*] \quad (1)$$

Table 1. Absorption characteristics of phenylallenes ($C_6H_5CH{=}C{=}CHR$); band assignments and comparisons with the results of CNDO/S-(SE + DE)-CI calculations

	Experimental					Theoretical			
State	$\tilde{\nu}$/cm^{-1}	ε / l mol^{-1} cm^{-1}	Comment	ΔE/eV	f^{b}	$\Delta\tilde{E}$/eV^{g}	$\tilde{f}$	DE (%)^{c}	CI Composition^{d,e}
(**1**) (R = MeO)^{a}									
[S_0						−0.89		7.7	−0.96 (0, 0) +0.18 (2731, 2731)]
S_1	30 000^{f}	83	E.f./m.a.	3.72	4.6×10^{-2}	4.28 (3.78)^{g}	9.1×10^{-5}	4.7	−0.80 (27, 29) −0.55 (27, 32)
S_2	32 500	146	E.f./m.a.	4.03	5.9×10^{-2}	4.79 (4.17)	1.0×10^{-4}	5.8	−0.90 (28, 31) +0.35 (25, 31)
S_3	34 400	484	(0–0) transition	4.26	0.0099	5.13 (4.43)	0.0072	4.2	+0.78 (28, 30) +0.56 (26, 29)
	35 500								
	35 900								
	37 000								
S_5	39 400^{f}	5 460	Tentatively by comparison with S_5 of (**8**) and (**9**)	4.88		6.51 (5.48)	0.023	16.4	0.77 (28, 32) −0.34 (2829, 2829)
S_4	40 100	10 400	1 100 cm^{-1} Vibrational progression not observed for (**8**), but for (**2**)	4.97	0.37	5.50 (4.71)	1.10	0.9	−0.90 (28, 29) +0.36 (27, 31)
	41 200	10 300							
S_6	43 000^{f}	7 600	At the same position (**8**) has an m.a./e.f. transition governing its c.d. spectrum, probably buried by strong bands			6.55 (5.51	1.9×10^{-4}	12.1	0.92 (17, 29) −0.24 (2729, 2830)$^{5]}$
S_7						6.65 (5.58)	0.0	99.8	−0.75 (2729, 2831)$^{4]}$ −0.43 (2729, 2831)$^{5]}$
S_8	45 300	5 070							
	46 800	7 500		5.80	0.32	6.87 (5.75)	0.63	4.9	−0.75 (26, 29) +0.56 (28, 30)
S_9			Probably buried by strong bands			7.02 (5.87)	1.0×10^{-4}	9.0	−0.70 (27, 32) +0.48 (27, 29)
S_{10}	48 700	17 600							
	49 400	18 800		6.12	0.48	7.17 (5.98)	0.48	7.9	−0.80 (26, 30) +0.45 (25, 29)
(**3**) (R = CN)^{h}									
[S_0						−0.70		6.4	0.97 (0, 0) −0.14 (2429, 2429)]
S_1	30 770	1 790	Much more intense than the corresponding bands of (**1**), (**2**), (**7**)—(**9**) ($\varepsilon \approx$ 10—100);^{2,4,13} two states	3.81	0.018	4.27 (3.78)	1.1×10^{-4}	3.8	0.89 (26, 29) −0.35 (23, 29)
S_2						4.56 (4.00)	7.4×10^{-5}	4.4	0.84 (24, 27) +0.45 (24, 30)
S_3	35 840	3 630	Without typical vibrational structure as in (**1**); comprises at least one further state^{i}	4.44	0.012^{j}	4.96 (4.30)	0.0014	4.7	−0.62 (25, 27) −0.73 (26, 28)
S_4	40 800	8 000		5.06	0.08	5.20 (4.48)	1.18	1.9	−0.87 (26, 27) −0.42 (24, 29)
S_5	35 840	3 630	C.t. character	4.44	0.024^{j}	5.48 (4.69)	3.1×10^{-4}	1.0	−0.82 (24, 31) −0.49 (19, 31)
S_6						6.15 (5.20)	0.0013	0.1	−0.72 (22, 29) −0.54 (22, 32)
S_7	39 500^{f}	4 890	May be vibrational component of S_4 or by comparison with (**1**) and (**9**) a separate state (E_{2g})	4.90	0.049	6.40 (5.39)	0.022	13.8	0.77 (26, 30) −0.34 (2627, 2627)
S_8	45 000	9 340		5.64	0.094	6.50 (5.47)	0.59	5.2	−0.71 (25, 27) +0.59 (26, 28)
S_9	42 600	8 030	C.t. character	5.28		6.65 (5.58)	5.4×10^{-5}	15.1	−0.91 (25, 29) +0.27 (2529, 2629)
S_{10}	50 760	26 095		6.29	0.13^{k}	6.79 (5.69)	0.31	8.4	0.47 (25, 28) +0.60 (24, 29)
S_{11}	45 000	9 340	C.t. character	5.64		6.80 (5.70)	4.1×10^{-4}	13.6	0.90 (24, 28) +0.23 (2427, 2628)$^{5]}$
S_{12}	50 760	26 095		6.29	0.13^{k}	7.12 (5.94)	0.10	13.9	0.69 (25, 30) −0.41 (23, 28)

Table 1 (*continued*)

	Experimental					Theoretical			
State	$\tilde{\nu}$/cm^{-1}	ε l mol^{-1} cm^{-1}	Comment	ΔE/eV	f[b]	$\Delta\tilde{E}$/eV[g]	$\tilde{f}$	DE (%)[c]	CI Composition[d,e]
(2) (R = CO_2H)[l]									
[S_0						−0.66		6.0	−0.97 (0, 0) +0.14 (2933, 2933)]
S_1	32 000[m]	58		3.97	3.0×10^{-4}[p]	4.84 (4.21)	9.9×10^{-5}	4.4	0.86 (28, 31) −0.47 (28, 34)
S_2	34 000[m]	800		4.22	4.8×10^{-3}[p]	4.10 (3.65)	2.2×10^{-4}	3.4	0.87 (30, 32) +0.29 (27, 32)
S_3	35 600[n]	1 450		4.41	0.0030[p]	4.92 (4.27)	0.0015	4.7	0.62 (29, 31) −0.73 (30, 33)
S_4	40 500[n]	17 450		5.02	0.23[p]	5.24 (4.51)	1.18	1.5	−0.89 (30, 31) +0.40 (28, 32)
S_5						5.56 (4.76)	0.0058	0.0	−0.51 (27, 32) −0.45 (26, 32)
S_6	39 000[m]	12 600		4.84		6.35 (5.36)	0.016	14.9	0.78 (30, 34) −0.35 (3031, 3031)
S_7	45 250[m]			5.61	0.034[p]	6.55 (5.51)	0.58	5.3	−0.71 (29, 31) −0.59 (30, 33)
S_8	43 000[m]			5.33	0.012[p]	6.57 (5.52)	4.0×10^{-4}	14.9	−0.91 (29, 32) −0.27 (2931, 3032)$^{5]}$
S_9	46 600[m]			5.78	0.22[p]	6.84 (5.73)	0.52	6.6	−0.52 (28, 32) −0.65 (29, 33)
S_{10}						7.00 (5.85)	3.6×10^{-4}	10.7	0.87 (28, 33) −0.26 (24, 33)
S_{11}	47 200[o]			5.85	0.24[b]	7.06 (5.90)	0.078	14.3	−0.70 (29, 34) +0.38 (29, 36)
S_{12}						7.13 (5.95)	0.093	3.7	0.54 (26, 31) −0.29 (29, 33)
S_{13}	48 800[n]	32 500		6.05	0.32[p]	7.22 (6.02)	0.17	13.5	0.42 (30, 36) +0.40 (28, 32)

[a] HOMO $\pi_{(1)}$ (28), LUMO $\pi_{(1)}{}^*$ (29). [b] Estimated according to lg f ≈ lg ε − 5. [c] Overall contributions from DE configurations in the CI expansions. [d] Only the two leading terms are given. [e] For the notation 4] and 5] *cf.* footnote *e* in Table 2 in ref. 2. [f] Shoulder or inflection, respectively. [g] Values in parentheses are from the correlation $\Delta E = 0.79\Delta\tilde{E} + 0.53$.[2] [h] HOMO $\pi_{(1)}$ (26), LUMO $\pi_{(1)}{}^*$ (27). [i] Three times more intense than corresponding band of (**2**). [j] As an approximation one third of the absorption intensity (ε ≈ 1 200) is attributed to S_3 [*cf.* (**1**) and (**3**)] and two thirds (ε ≈ 2 400) to S_5 and S_6. [k] Half the intensities are attributed to S_{10} and S_{12}, respectively. [l] HOMO $\pi_{(1)}$ (30), LUMO $\pi_{(1)}{}^*$ (31). [m] From the c.d. data of (**10**) or (**11**), respectively. [n] From the absorption spectrum of (**2**).[4] [o] From low-temperature absorption spectra of phenylallenecarboxylic acids.[4] [p] From the dipole strengths D_{0i} given in ref. 4 using the equation $f_{0i} = 4.7 \times 10^{29}\ \tilde{\nu}_{0i}\ D_{0i}$.

Table 2. Summary of characteristics of electronic excited states of phenylallenes with first-row substituents

Energy (cm^{-1})	State	Compound	Characteristic features	Localization properties	Substituent effects	DE (%)	Leading terms (electronic configurations)
28 000 to 33 000	S_1, S_2	All	M.a./e.f.	Essentially allenic moiety	Small	3—6	$[\bar{\pi}_{(1)},\pi_{(1)}{}^*]$, $[\pi_{(1)},\bar{\pi}_{(1)}{}^*]$
34 500	S_3	All	Characteristic vibrational structure [exception: (**3**)]	Essentially benzene ring ($^1B_{2u}$)	None	3—6	
40 000	S_4	(**1**)—(**3**) (**7**)—(**9**)	Approximately described by equation (1), state of special interest	Strongly delocalized ($^1B_{1u}$-benzene + $^1B_2$-allene + c.t. components)[2,4]	Bathochromic shifts by donors [(**1**), (**8**), (**9**)]; hypsochromic by acceptors [(**2**), (**3**)]	1—2	$[\pi_{(1)},\pi_{(1)}{}^*]$, $[\bar{\pi}_{(1)},\bar{\pi}_{(1)}{}^*]$
39 000	S_5			$^1E_{2g}$ of benzene	Small	15	$[\pi_{(1)},\pi_{(3)}{}^*]$, $[\pi_{(1)}\pi_{(1)}{}^*,\pi_{(1)}\pi_{(1)}{}^*]$
43 000			M.a./e.f., induces characteristic c.d. features of phenylallenes		Donors: (**1**), (**8**); acceptors: (**2**), (**3**)	12—15	$[\bar{\pi}_{(1)},\pi_{(2)}{}^*]$; $[\pi_{(2)},\bar{\pi}_{(1)}{}^*]$
44 000		(**1**), (**8**), (**9**)	State was assigned for (**9**)[2]			99.9	$[\bar{\pi}_{(1)}\pi_{(1)}{}^*,\pi_{(1)}\bar{\pi}_{(1)}{}^*]$
46 000		(**1**)—(**3**), (**7**)—(**9**)		$^1E_{1u(a)}$ of benzene or toluene Toluene	None	5	
49 000		(**1**), (**8**)	Compounds with donors	$^1E_{1u(b)}$		5	
50 000		(**2**), (**3**)	Compounds with acceptors, several states of which are mixtures	$^1E_{1u(b)}$ (benzene), $[\bar{\pi}_{(1)},\bar{\pi}_{(1)}{}^*]$ (allene)		>10	

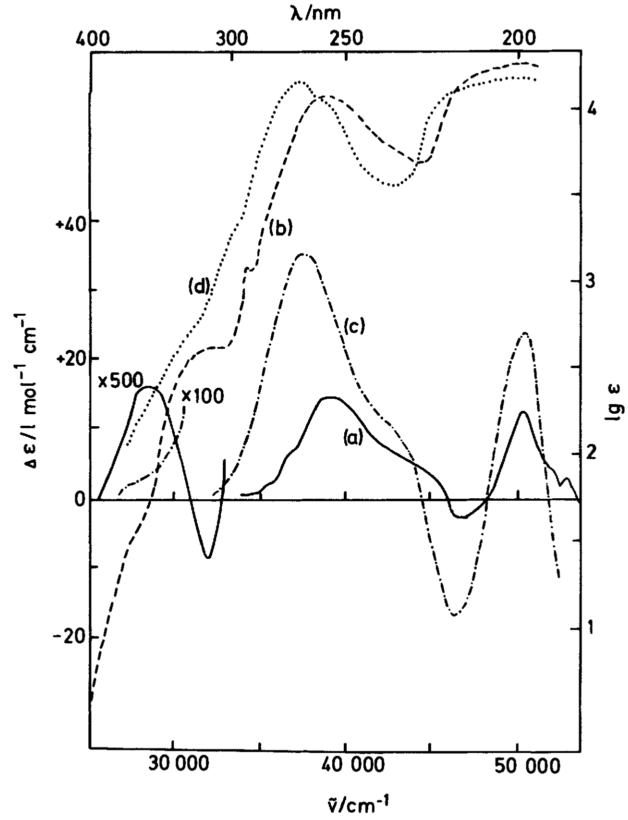
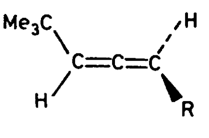


Figure 2. Circular dichroism (c.d.) and u.v. absorption spectra of 3-chloro-1-phenylallene (**4**) [(a) c.d., (b) u.v.] and 3-bromo-1-phenylallene (**5**) [(c) c.d., (d) u.v.]

phenylallenes (**1**)—(**3**) [and (**7**) and (**8**)][2] the calculated energies of S_4 have rather large errors. As the overall variation of S_4 in the series amounts to only 1 400 cm^{-1} (0.17 eV), it is not surprising that the CNDO/S scheme cannot reproduce the trend for the experimental spectral position of S_4. This trend is a bathochromic shift for compounds with donors [(**1**), (**8**), and (**9**)] relative to (**7**) ($\tilde{\nu}$ = 40 400 cm^{-1})[13] and a hypsochromic shift for phenylallenes with acceptors [(**2**) and (**3**)].

As the difference between the S_4 band positions of compounds with a very strong donor [(**1**)] and a very strong acceptor [(**3**)] is only 700 cm^{-1} [*cf.* 4 900 cm^{-1} between S_4 of (**7**) and (**6**)] one can assume that the π-donor/acceptor properties of the 3-substituents do not enter as relevant contributions to the overall substituent effect on S_4. Furthermore, the field effects exerted by the groups' dipole moments μ(R) can also play only a minor role, *e.g.* the substitution for a methyl group [$\mu(CH_3)$ = −0.4 D][8] of a cyano group [μ(CN) = 4.28 D][8] is associated with a small (hypsochromic) S_4-shift of 900 cm^{-1}.

3-*Halogeno*-1-*phenylallenes*.—For a series of halogeno derivatives (*e.g.* Cl, Br, or I) substituent effects are either small or there is a regular change in the particular property, *i.e.* one finds almost linear incremental changes in a series. Previously, this was shown to be valuable in the investigation of excited states of 3-t-butylallenes (**15**)—(**17**).[6] In Figures 2 and 3 the c.d. and u.v. spectra of the 3-halogeno-1-phenylallenes (**4**)—(**6**) are given.



	(**15**)	(**16**)	(**17**)
R =	Cl	Br	I

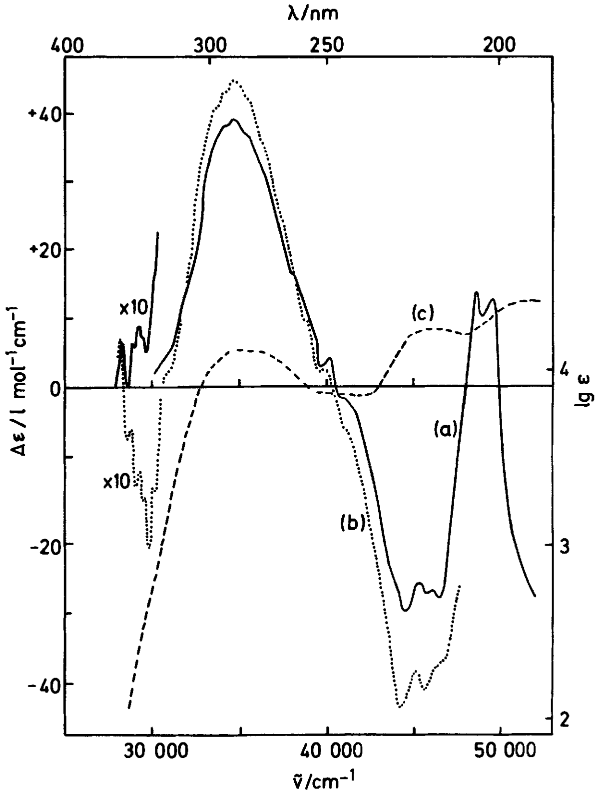


Figure 3. Circular dichroism (c.d.) [(a) *T* 298 K, (b) *T* 133 K] and (c) u.v. absorption spectra of 3-iodo-1-phenylallene (**6**)

The most remarkable feature is the bathochromic shift of the lowest-energy intense u.v. bands from 38 900 [(**4**)] to 35 460 cm^{-1} [(**6**)]. The u.v. intensities of these bands remain almost unchanged, whereas the c.d. intensities are increased by a factor of three in going from Cl to I.

In contrast to the u.v. spectra the c.d. spectra of (**4**)—(**6**) provide a wealth of information about electronic bands which contribute to the spectral range of interest.

Empirical band assignments. In Table 3 the c.d. and u.v. characteristics of the allenes (**4**)—(**6**) together with band assignments are presented as a comparative summary. As usual and in particular clearly seen for (**4**) (Figure 2), at lowest energy two bands are found which can be related to states S_1 and S_2 resulting from m.a., e.f. transitions. As S_1 and S_2 are localized essentially at the C=C=C skeleton, it is not surprising that the c.d. shapes of S_1 and S_2 for (**4**)—(**6**) are very similar to those of the 3-t-butylallenes (**15**)—(**17**).[6]

The lowest-energy state $S_1[\bar{\pi}_{(1)},\pi_{(1)}^*]$ of phenylallenes correlates with $S_1[\pi_{(1)},\bar{\pi}_{(1)}^*]$ in monosubstituted allenes H_2C=C=CHR[7,14] or 3-alkyl-1-substituted allenes AlkHC=C=CHR, such as (**15**)—(**17**),[6] respectively [the $\pi_{(1)}$ (C=CHR) orbital in H_2C=C=CHR becomes $\bar{\pi}_{(1)}$ in phenylallenes!]. For phenylallenes with R = MeO, CO_2H, CN, or Bu^t, $S_1[\bar{\pi}_{(1)},\pi_{(1)}^*]$ is found (6 400 ± 450) cm^{-1} to the red of the corresponding excited states of simple allenes. For the halogeno(phenyl)allenes (R = Cl, Br, or I), however, this shift amounts to 8 900 ± 1 000 cm^{-1}. This is a hint at the exceptional role of halogeno substituents in the phenylallene series.

In the room-temperature c.d. spectrum of (**6**) (Figure 3), 250 and 430 cm^{-1} vibrational progressions appear in the lowest energy bands. On the other hand, in the low-temperature c.d. spectrum (Figure 3), after three 410 cm^{-1} vibrational progressions, two 330 cm^{-1} progressions are seen. The iodo compound (**17**) exhibits 360 and 580 cm^{-1} progressions.[6] With

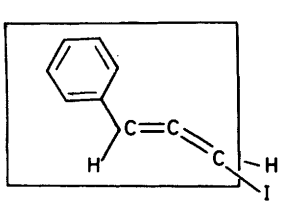
Table 3. C.d. and u.v. absorption characteristics of 3-halogeno-1-phenylallenes $C_6H_5CH{=}C{=}CHR$

State	R = Cl (4)		R = Br (5)		R = I (6)	
	$\tilde{\nu}_{c.d.}$ ($\tilde{\nu}_{u.v.}$) / cm^{-1}	$\Delta\varepsilon$ / $l\ mol^{-1}\ cm^{-1}$	$\tilde{\nu}_{c.d.}$ ($\tilde{\nu}_{u.v.}$) / cm^{-1}	$\Delta\varepsilon$ / $l\ mol^{-1}\ cm^{-1}$	$\tilde{\nu}_{c.d.}$ ($\tilde{\nu}_{u.v.}$) / cm^{-1}	$\Delta\varepsilon$ / $l\ mol^{-1}\ cm^{-1}$
S_1 [$\bar{\pi}_{(1)},\pi_{(1)}$*]	28 500 (28 000)	$+3.2 \times 10^{-2}$	28 500	$+3.2 \times 10^{-2}$	28 250	+0.63
S_2 [$\pi_{(1)},\bar{\pi}_{(1)}$*]	32 000 (32 000)	-1.7×10^{-2}			31 000	+5
S_3 (B_{2u})	34 500 (34 200)	+0.72	(34 000)		*a*	
	35 500	+1.82				
	36 800	+6.5				
S_4 (B_{1u})	39 030 (38 900)	+14.65	37 650 (37 300)	+35.6	34 200	+38.0
					34 800	+39.0
					35 500 (35 460)	+36.5
S_5 (E_{2g})			(38 500)		38 000	+16.5
S_6 [$\bar{\pi}_{(1)},\pi_{(2)}$*]	42 000	+7	42 000	+12.5	40 600[b,c] (40 000)[d]	+4.2
					41 000[c]	−1.7
S_7 [$\bar{\pi}_{(1)},\sigma_{C-R}$*]	44 000	+5	44 000	<0	44 450	−29.3
S_8 [$E_{1u(a)}$]	47 000 (48 000)	−2.5	46 380 (45 000)	−16.7	45 700 (45 900)	−27.3
					46 500	−29.9
S_9 [$E_{1u(b)}$]	50 250 (50 000)	+12.4	50 450 (50 000)[e]	+23.8	(52 000)	<0
S_{10} (n_R,σ_{C-R}*)	52 000	+3.7	49 000[e]	(+10)[f]	48 590	+13.7
	52 900	+3.0			49 650	+12.6

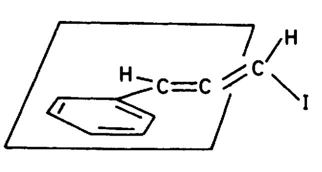
[a] Overlap of S_3 and S_4. [b] The regular vibrational progression in the low-temperature c.d. spectrum of (6) ($\tilde{\nu}$ = 1 000 cm^{-1}) indicates that around 40 000 cm^{-1} only one electronic band exists with a positive c.d., as is found for (4). [c] S-Shaped pair of c.d. bands. [d] Plateau. [e] The onset of the lowest-energy positive c.d. band goes through the corresponding positive double-humped c.d. band of (6). We, therefore, assume the 50 450 cm^{-1} c.d. band of (5) with double the intensity of the corresponding band of (4) to result from two overlapping bands. [f] Estimated value.

the exception of the lowest-energy vibrational band, upon cooling the c.d. of all the other vibrational bands reverses its sign. A corresponding sign inversion of the lowest-energy c.d. upon cooling was observed for (9).[2] Apparently comparable sign inversions of m.a., e.f. transitions upon cooling are observed, for instance, in the (n,π*) c.d. bands of adamantanones.[15] The situation for allenes, however, is more complicated. The (n,π*) band of saturated carbonyl compounds is energetically well separated from the other electronic bands. For the allenes there are two close-lying excited states which may couple vibronically in a non-adiabatic way.[2]

As the c.d. maximum of S_1 is reached for the fifth vibrational member the excitation of (6) into the S_1 (and probably also the S_2) state is presumably associated with considerable geometrical deformations. Following the suggestions for (9)[2] and (17),[6] we attribute the vibrational modes in the lowest-energy band of (6) to C=C=C bending. Furthermore, as for (9),[2] we suggest that the vibrational modes will generate preferentially the bending-in-plane *trans*-form (bip-*t*) and bending-out-of-plane *cis*-form (bop-*c*) of (6).



bip-*t*



bop-*c*

As for the the allenes (1), (2),[4] and (8) and (9),[2] S_1 and S_2 are followed by the B_{2u} band with a 1 100 cm^{-1} vibrational progression and a 0–0 transition near 34 500 cm^{-1} (S_3). The corresponding band is observed only for (4) (Figure 2). For (5) and (6) $S_3(B_{2u})$ is buried by the strong $S_4(B_{1u})$ band. The S_4 c.d. band of (6) has a vibrational structure. The low-temperature c.d. spectrum (Figure 3) reveals 450 cm^{-1} progressions to the red of the maximum (at 34 700 cm^{-1}) and a 900 cm^{-1} vibrational progression to the blue region. Vibrational progressions of 400 cm^{-1} in the S_4 and S_5 bands were also observed in the low-temperature c.d. and u.v. spectra of (9).[2] The 400 cm^{-1} modes of (6) are attributed to C=C=C bendings, whereas the 900 cm^{-1} mode is tentatively associated with the symmetric C=C=C stretch [$\tilde{\nu}_s$(C=C=C) = 1 076 cm^{-1} for $H_2C{=}C{=}CHI$].[16]

The shoulder at 38 500 cm^{-1} in the u.v. spectrum of the bromo compound (5) is assigned to a separate band and not to a vibrational component of the strong 37 300 cm^{-1} absorption band. This is supported by a shoulder in the room-temperature c.d. spectrum of (6) (Figure 3) at almost the same position. This shoulder of (6) is separated by at least 2 500 cm^{-1} from S_4 and, hence, is definitely a separate band. As (8) and (9) have their $S_5(E_{2g})$ states around 39 000 cm^{-1}, the 38 000 cm^{-1} bands of (5) and (6) are attributed to corresponding states. The existences of these states S_4 and S_5 can account for the broadening of the absorption bands of (5) and (6) relative to their c.d. bands.

The next excited state (S_6) in the series (4)—(6) is found near 42 000 cm^{-1}. Such a state is clearly seen as a distinct shoulder for (5) (Figure 2). The very slow decline of the S_4/S_5 c.d. band of (4) (Figure 2) giving a broad positive c.d. feature between 40 000 and 46 000 cm^{-1} suggests that the chloro compound (4) has two positive c.d. bands near 42 000 and 44 000 cm^{-1}.

In the absorption spectrum of (6) the plateau around 42 000 cm^{-1} indicates an electronic band at that position. On the other hand, the c.d. of (6) shows an S-shaped feature with a positive band at 40 060 and a negative one at 41 000 cm^{-1}. In the low-temperature c.d. spectrum of (6) two positive vibrational bands are seen ($\Delta\tilde{\nu}$ = 1 100 cm^{-1}). A third vibrational member at 41 000 cm^{-1} in the negative c.d. region is surely the result of overlap of the structured positive S_6 band with the negative S_7 band. As (1), (8), and (9), with donor substituents, show a [$\bar{\pi}_{(1)},\pi_{(2)}$*] excitation at 43 000 cm^{-1}, we suggest that S_6 of (4)—(6), which also have donor substituents, results from a corresponding transition.

For the S_7 bands the rise of the absorption coincides with the onset of strong negative c.d. bands in (5) (Figure 2) and (6) (Figure 3). Comparison of the c.d. spectra of (4) and (5) (Figure 2) indicates that the intense negative c.d. band of (5) comprises

Table 4. Theoretical (CNDO/S) and experimental excited-state energies and transition intensities of 3-chloro-1-phenylallene (**4**)

	Experimental		CNDO/S with Cl 3*d*[a]	CNDO/S without Cl 3*d*[b]			
State	ΔE/eV	f	$\Delta\tilde{E}$/eV	$\Delta\tilde{E}$/eV[e]	f	DE (%)	CI Composition[c,d]
S_0			0.0	−0.83		6.9	0.96 (0, 0) −0.16 (2328, 2328)
S_1 $[\bar{\pi}_{(1)},\pi_{(1)}^*]$	3.53	4×10^{-4}[h]	3.92	4.41 (3.88)	9.2×10^{-4}	6.2	0.86 (23, 26) +0.43 (23, 29)
S_2 $[\pi_{(1)},\bar{\pi}_{(1)}^*]$	3.97	4×10^{-3}[h]	3.89	4.74 (4.13)	1.3×10^{-4}	4.9	0.90 (25, 28) −0.37 (22, 28)
S_3 (B_{2u})	4.28	0.01[i]	4.37	5.08 (4.39)	0.0014	4.6	0.62 (24, 26) +0.73 (25, 27)
S_4 (B_{1u})	4.84	0.2[i]	4.61	5.44 (4.66)	1.10	1.2	0.93 (25, 26) −0.30 (23, 28)
S_5 (E_{2g})	4.71[f]	0.04[i]	5.97	6.55 (5.51)	0.0023	14.8	0.77 (25, 29) +0.36 (2526, 2526)
S_6 $[\bar{\pi}_{(1)},\pi_{(2)}^*]$	5.21	0.02[i]	6.48	6.77 (5.68)	9.7×10^{-4}	15.0	0.90 (23, 27) −0.25 (2326, 2527)$^{5]}$
S_7 $[\bar{\pi}_{(1)},\sigma_{C-Cl}^*]$	5.45		6.26	6.49 (5.46)	0.037	1.7	0.42 (23, 30) −0.31 (23, 31)
$[\bar{\pi}_{(1)}\pi_{(1)}^*,\pi_{(1)}\bar{\pi}_{(1)}^*]$				7.05 (5.89)	8.0×10^{-6}	99.2	−0.75 (2326, 2528)$^{4]}$ −0.43 (2326, 2528)$^{5]}$
S_8 $[E_{1u(a)}]$	5.83	0.10[i]	6.49	7.09 (5.92)	0.55	4.8	0.44 (22, 26) −0.81 (24, 27)
$[\pi_{(2)},\bar{\pi}_{(1)}^*]$				7.25 (6.04)	2.4×10^{-5}	17.5	0.91 (24, 28) −0.29 (2426, 2528)$^{5]}$
S_9 $[E_{1u(b)}]$	6.23	0.2[i]	5.79	7.26 (6.05)	0.086	13.9	0.71 (24, 29) +0.42 (22, 27)
S_{10} (n_{Cl},σ_{C-Cl}^*)	6.45		*g*	*g*			

[a] SE-CI level. [b] (SE + DE)-CI level; for the notation 4] and 5] see ref. 2. [c] Only the two leading terms are given. [d] HOMO $\pi_{(1)}$ (25), LUMO $\pi_{(1)}^*$ (26). [e] Values in parentheses are from the correlation $\Delta E = 0.76\Delta\tilde{E} + 0.53$.[2] [f] From compounds (**5**) and (**6**) (Table 2). [g] The energy of the (n_{Cl},σ_{C-Cl}^*) configuration is beyond the energetic limit used for the CI procedure and, therefore, this state does not appear among the CI states [for $H_2C{=}C{=}CHCl$ one finds $\Delta E(n_{Cl},\sigma_{C-Cl}^*) = 6.12$ eV, if Cl 3*d* atomic orbitals are included].[14] [h] Estimated from lg f ≈ lg ε − 5. [i] Estimated from comparisons with data for (**9**).[2]

two bands (at *ca.* 44 000 and 46 380 cm^{-1}). The lower-energy c.d. band of (**5**) corresponds to the positive c.d. band of (**4**) around 44 000 cm^{-1}. Hence, the c.d. becomes increasingly more negative for the series R = Cl, Br, I. In that spectral region the same c.d. feature is observed for (**15**)—(**17**).[6] Following the assignments for these last compounds, S_7 is associated with a state resulting from the $[\bar{\pi}_{(1)},\sigma_{C-R}^*]$ excitation. The virtual C–R σ orbital contains considerable contributions from halogen *d* atomic orbitals.[6,14]

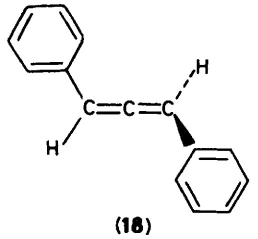
For energetic reasons the negative c.d. feature at *ca.* 46 500 cm^{-1} for (**4**)—(**6**) is assigned to the $E_{1u(a)}$ state [*cf.* also (**8**)].[2] The $S_8[E_{1u(a)}]$ state has a rather large electric transition moment. In (**6**) the strong absorption band of S_8 is separated from the highest-energy strong u.v. band. In the S_8 c.d. band of (**6**) a 800 cm^{-1} vibrational progression appears.

The strong absorption maxima of (**4**)—(**6**) around 50 000 cm^{-1} are assigned to the second state $[E_{1u(b)}]$ correlating with $^1E_{1u}$ in benzene. These u.v. maxima correspond to positive c.d. bands for (**4**) and (**5**) (Figure 2), but a negative one for (**6**) (Figure 3).

The positive c.d. band of the iodo compound (**6**) at 48 590 cm^{-1} with a 1 050 cm^{-1} progression coincides with the rise of the strong positive c.d. band of (**5**). The 50 450 cm^{-1} c.d. band of (**5**) has double the intensity of the corresponding band of (**4**). Therefore, one can hypothesize that this band of (**5**) comprises two c.d. bands of almost equal intensities, $S_9[E_{1u(b)}]$ and S_{10} (at 52 000 cm^{-1}).

The S_{10} band of the chloroallene (**4**) is found to the blue of $S_9[E_{1u(b)}]$ (Figure 2). This assignment is confirmed by the fact that the 52 000 cm^{-1} c.d. band of (**4**) exhibits the same double-humped feature as does the 48 590 cm^{-1} band of (**6**) and, furthermore, has almost the same vibrational progression (900 cm^{-1}). The S_{10} bands of (**4**)—(**6**) are found at the positions where for (**15**)—(**17**) the (n_R,σ_{C-R}^*) excitations are found.[6] As (n_R,σ_{C-R}^*) is localized essentially at the C=C–R subunit, a corresponding assignment for the S_{10} bands of (**4**)—(**6**) is reasonable.

In connection with the empirical treatment of excited states of phenylallenes a final remark concerning emission properties of phenylallenes seems worthwhile. For emission properties of molecules the nature of the lowest-energy excited singlet states is important. As S_1 and S_2 of phenylallenes result from electrically forbidden transitions and generate very weak absorption bands, the lifetimes τ (τ ≈ 1/f) of these states will be sufficiently long that intersystem crossing (or other non-radiative and photochemical deactivation pathways) will deplete these states before fluorescence can occur. Thus no fluorescence was detected for (**9**)[2] and 1,3-diphenylallene (**18**).[17] Similarly, when the chloro- and bromo-phenylallene (**4**) and (**5**) were irradiated in n-hexane at 290, 285, and 260 nm at room temperature, no fluorescence was detected. Also, at 90 K (in 1:3 methylcyclohexane–isopentane) fluorescence was absent.



(**18**)

CNDO/S Computations. The empirical assignments of electronic bands for the halogeno(phenyl)allenes are supported by the results of CNDO/S calculations for the chloroallene (**4**) (Table 4). On the one hand, CNDO/S-SE-CI calculations including *d* atomic orbitals were performed; on the other, as for (**1**)—(**3**), (SE + DE)-CI calculations neglecting Cl *d* atomic orbitals were carried out.

For the low-energy part (3.5—4.8 eV) the (SE + DE)-CI calculations for (**4**) give the correct sequence of excited states (S_1 − S_4). In particular, the corrected theoretical values (in parentheses) show sufficient agreement with the experimental ones. The results of the SE-CI calculations including *d* atomic orbitals are comparable in quality except for the prediction that the two lowest-energy excited states are almost degenerate. The calculations show that S_4 of (**4**) does not contain any significant contribution from DE configurations and exhibits a mixture of $[\pi_{(1)},\pi_{(1)}^*]$ and $[\bar{\pi}_{(1)},\bar{\pi}_{(1)}^*]$ configurations similar to that found for (**1**)—(**3**), (**7**), and (**8**)[2] [equation (1)].

For the energetic range 4.8—6.0 eV the SE-CI calculations reverse the sequence of the close-lying states S_6 and S_7. The (SE + DE)-CI scheme shifts S_7 even to the red of S_5. As usual[2] the energetic splitting and the sequence of $S_4(B_{1u})$ and $S_5(E_{2g})$ cannot be reproduced by vertical excitation energy calculations. As for the other phenylallenes the position of $S_5(E_{2g})$ is *ca.* 0.8 eV from the corrected theoretical value (in parentheses).

On the (SE + DE)-CI level an excited state is predicted to exist at the position of $S_8[E_{1u(a)}]$. Such a state was not detected for any of the compounds **(4)**—**(6)**. This state is generated only by DE configurations and was assigned for **(9)** to a band at 5.53 eV. In **(9)** this DE state induces a c.d. with the same sign as has $E_{1u(a)}$. Hence, it may be that such a state contributes to the broad positive c.d. feature of **(4)** between 5.2 and 5.7 eV. A further excited state, $[\pi_{(2)},\bar{\pi}_{(1)}^*]$, is predicted to exist in the S_8/S_9 spectral region. This raises the question as to whether the structures in the high-energy negative and positive c.d. bands of **(6)** are indeed of vibrational origin (as suggested) or correspond to different electronic bands, one being the $[\pi_{(2)},\bar{\pi}_{(1)}^*]$ state predicted by the (SE + DE)-CI calculations.

The SE-CI calculation reverses the sequence of the $E_{1u(a)}$ and $E_{1u(b)}$ states. For both types of calculation the CI truncation results in the omission of the (n_{Cl},σ_{C-Cl}^*) configuration which is the essential contribution to S_{10}. Hence, there is no theoretical support for the assignment of S_{10} of **(4)**. However, theoretical results for chloroallene ($H_2C=C=CHCl$) corroborate the assignment of S_{10} (*cf.* footnote *g* in Table 4).

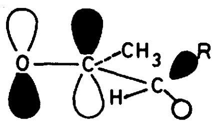
The CNDO/S calculations including Cl 3*d* atomic orbitals for **(4)** show that the LCAO expansions contain small contributions from chlorine *d* atomic orbitals. These, together with the 2*s* and 2*p* atomic orbitals, can be interpreted as small admixtures of the C–Cl orbitals σ_{C-Cl} and σ_{C-Cl}^* into $\pi_{(1)}$ and $\pi_{(1)}^*$, respectively, and can be characterized as π-type hyperconjugations.[9] Furthermore, in the occupied orbital also mixing between $\pi_{(1)}$ and the 'lone pair' n_{Cl} is operative $[\pi_{(1)}/n_{Cl}$ hyperconjugation]. A corresponding $\pi_{(1)}/n_I$ hyperconjugation was detected in the photoelectron spectrum of **(17)**.[6]

Inclusion of Cl 3*d* atomic orbitals has a negligible effect on the energies of the $\pi_{(i)}$, $\bar{\pi}_{(i)}$, n_{Cl}, and σ_{C-Cl} orbitals. Only the energy of the virtual orbital σ_{C-Cl}^* is affected. Relative to the value if *d* atomic orbitals are neglected, σ_{C-Cl}^* is stabilized by *ca.* 1 eV. Correspondingly, the CNDO/S excited-state energies without incorporation of *d* atomic orbitals do not differ significantly from those with inclusion of such orbitals. Excited-state energies where the corresponding electronic transitions terminate at σ_{C-Cl}^*, on the other hand, are strongly reduced.

From the LCAO expansions of the orbitals one can see that for **(1)** and **(3)** also, π-type hyperconjugations are operative in $\pi_{(1)}$ and $\pi_{(1)}^*$. The contributions from the C–R (R = MeO or CN) occupied and unoccupied orbitals, however, are small. For **(2)** the CNDO/S calculation shows the 'through-bond' interaction of the $\pi_{(1)}$ allenic orbital and the carboxy n_O orbital, observed in the photoelectron spectrum of $H_2C=C=CHCO_2Me$.[14]

Though the CHR hyperconjugations in the LCAO expansions are larger for **(4)** (R = Cl) than for the other phenylallenes, the CNDO/S calculations do not give final evidence that the observed distinct bathochromic S_4 shifts of **(4)**—**(6)** are essentially influenced by the halogen *d* atomic orbitals, in particular, $\pi_{(1)}^*/\sigma_{C-Cl}^*$ hyperconjugations.

Comparison of the situation of the phenylallenes with the (n,π^*) u.v. band shifts of heterosubstituted acetones RCH_2COCH_3, however, seems to support the suggestion that $\pi_{(1)}^*/\sigma_{C-Cl}^*$ hyperconjugation is important for the S_4 band shift. For RCH_2COCH_3, distinct bathochromic (n,π^*) band shifts are observed for R = Cl, Br, or I.[18] These shifts were interpreted primarily in terms of $\pi_{CO}^*/\sigma_{C-R}^*$ hyperconjugations in the *gauche* conformers of the acetones.[18,19] The *gauche* $\pi_{CO}^*/\sigma_{C-R}^*$ hyperconjugations, as visualized in **(A)**, can be compared with the CHR hyperconjugations between $\pi_{(1)}^*$ and σ_{C-R}^* in the phenylallenes. Since, as a result of the interaction with σ_{C-R}^*, the stabilization of the π_{CO}^* orbital increases with increasing atomic number of the halogen, the (n_O,π_{CO}^*) band shifts of the acetones were related to the decrease of the energy gap between n_O and π_{CO}^*.[18,19] In ref. 19, however, it was pointed out that the (n_O,π_{CO}^*) shift is not simply related to the decrease in the n_O–π_{CO}^* gap.



(A)

Applying the foregoing arguments to phenylallene means that the S_4 band shifts of **(4)**—**(6)** should be due essentially to a decrease in the $[\pi_{(1)},\pi_{(1)}^*]$ configuration as a result of favourable $\pi_{(1)}^*/\sigma_{C-R}^*$ hyperconjugation for the halogen compounds. In ref. 18 it was shown by a bivariate correlation that the (n_O,π_{CO}^*) band shift is influenced not only by $\pi_{CO}^*/\sigma_{C-R}^*$ hyperconjugation (represented by the polarizability $\bar{\alpha}$), but also by a field effect of the group R (represented by the inductive substituent constant σ_I). Use of the data for **(1)**—**(8)** as the basis shows that the S_4 band position $\tilde{\nu}(S_4)$ follows a similar correlation (2) with the group polarizabilities $\bar{\alpha}(R)$ (as defined in ref. 20) and the group electric dipole moments μ(R).[8] Correlation (2) is only of medium quality. However, in view of all the foregoing arguments and the hyperconjugative interactions observed in the ^{13}C n.m.r. chemical shifts of the phenylallenes,[9] it appears that hyperconjugation plays an important role in substituent effects on the S_4 band positions of 3-substituted phenylallenes.

$$\tilde{\nu}(S_4) = 41\,893 + 364\,\mu(R) - 1\,156\,\bar{\alpha}(R) \qquad (2)$$
$$[\mu(R) \text{ in D}, \bar{\alpha}(R) \text{ in Å}^3;\ R^2 = 0.8588,\ f = 0.38]$$

In a further paper, however, it will be shown[21] that the observed effect results from a complicated interplay of at least five distinct physical effects, and hyperconjugation is of varying importance for the different phenylallenes. In this paper,[21] furthermore, the breakdown of the simple model of viewing allenes as composed of two ethylenes will be demonstrated.

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