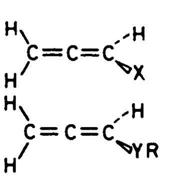
The Molecular Structure of Allenes and Ketenes. Part 19.[1] Photoelectron Spectra and Conformations of Donor-substituted Allenes

Johan Kamphuis and Hendrik J. T. Bos*
Laboratory of Organic Chemistry, State University, Croesestraat 79, 3522 AD Utrecht, The Netherlands
Cor W. Worrell
Laboratory of General Chemistry, State University, University Transistorium 3, Padualaan 8, 3508 TC Utrecht, The Netherlands
Wolfgang Runge*
Institut für Struktur- und System-forschung, Wormser Str. 5, D-6900 Heidelberg, W. Germany

He^I photoelectron (p.e.) spectra for the donor-substituted allenes $RCH{=}C{=}CH_2$ [R = $(CH_3)_3C$ (**1**), $N(CH_3)_2$ (**2**), OCH_3 (**3**), OC_2H_5 (**5**), $OC(CH_3)_3$ (**6**), SCH_3 (**4**), SC_2H_5 (**7**), $SC(CH_3)_3$ (**8**)] are reported and assignments of p.e. bands with energies $I_v < 12.5$ eV are presented. Substituent effects on the p.e. band positions can be interpreted in terms of intrinsic electronic effects of the groups R, vibronic coupling effects (of the Jahn–Teller or pseudo-Jahn–Teller-type, respectively) being negligible. Interactions of the substituents with the remote allenic C=C moiety are rationalized through Coulombic field effects and hyperconjugations. The lowest energy ionic states of (**1**)—(**8**) have geometries which deviate considerably from those of the neutral ground-state. In particular, ($\mathbf{2}^+$) and ($\mathbf{8}^+$) are shown to have bent C=C=C geometries. From the p.e. spectra it is inferred that compound (**2**) has a non-planar geometry. This is supported by MINDO/3 calculations. Furthermore, it is shown that all the radical cations exist in one largely preferred conformation. For the methyl and ethyl compounds (**3**), (**5**), (**4**), and (**7**) it is the *s-cis* conformation, whereas for the t-butyl molecules (**6**) and (**8**) the *s-trans* form is preferred.

Knowledge of molecular and electronic structures is basic for the rationalization of chemical reactions. A simple and successful resolution of this problem has been provided by the 'frontier molecular orbital approach'.[2] Accordingly, the kinetic and stereoselective dependence of a (thermal or photochemical) reaction is related to the energies (and wavefunction coefficients) of both the highest occupied (HO) and lowest unoccupied (LU) molecular orbitals. In particular, it has been shown[3,4] that the rates of the reactions of monosubstituted (or 1,1- and 1,3-disubstituted) allenes or aryl-substituted phenylallenes, respectively, with aromatic ketones and thioketones can be related to the ionization energies of the allenes' HOMOs.

U.v. photoelectron (p.e.) spectroscopy represents an appropriate means of obtaining information about orbital energies of occupied MOs and interactions between particular molecular skeletons and the substituents. In this paper the He^I p.e. spectra of the monosubstituted allenes (**1**)—(**8**) with a π-donor group are reported.



(1) X = $C(CH_3)_3$
(2) X = $N(CH_3)_2$
(3) X = OCH_3
(4) X = SCH_3
(5) Y = O, R = C_2H_5
(6) Y = O, R = $C(CH_3)_3$
(7) Y = S, R = C_2H_5
(8) Y = S, R = $C(CH_3)_3$

The interpretation of p.e. spectra of organic compounds usually relies on Koopmans' approximation (1). Here, the (experimental) vertical ionization energy $I_v(i)$ is related to the negative (ground-state) orbital energy ε_i^{SCF} calculated with an

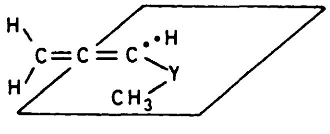
$$I_v(i) = -\varepsilon_i^{SCF} \qquad (1)$$

SCF procedure. For allenes, in particular, there are several (sometimes co-operative) effects which may complicate inferences to be made from the situations of radical cations to those of neutral molecules in the sense of equation (1). For allenes Koopmans' approximation (1) often loses its validity.[1,5–7] Its breakdown may be due to vibronic coupling, *i.e.* geometrical distortions of the cations and mixing of close lying orbitals as a result of non-adiabatic effects (in particular, Jahn–Teller (JT) and pseudo-JT-effects).[1,5–7] But also vibrational effects which can be understood in the context of the adiabatic approximation and the Franck–Condon principle may complicate interpretations of p.e. spectra of allenes.

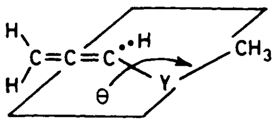
For radical cations the extent of vibronic coupling between two electronic states becomes smaller with increasing mesomeric abilities of the substituents (*i.e.* with increasing delocalization of the orbitals across the molecular skeleton and the substituents).[5,7] As the groups $N(CH_3)_2$ and OAlk are strong π-donors and SAlk are medium strong π-donors with large delocalization effects, one can anticipate that in the p.e. spectra of (**2**)—(**8**) vibronic (pseudo-JT) effects will play a small or negligible, respectively, role. With $(CH_3)_3C$ being a relatively weak donor probably only for (**1**) pseudo-JT-effects are operative. For the interpretations of the p.e. spectra of other alkylallenes the intrinsic (electronic) effect of the substituent and an effect due to vibronic coupling (JT- or pseudo-JT-effects) must be taken into account.[6]

Even within the limit of the validity of Koopmans' approximation (1) deductions of electronic effects of the substituents on the orbital energies of the considered allenes may be difficult due to the existence of conformer equilibria. For the compounds with singly bonded groups lacking (local) rotational symmetries, such as YCH_3 (Y = CH_2, O, S), several conformers may exist. Discussions of conformer equilibria of such compounds generally refer to *s-cis* (*c*; dihedral angle θ = 0°), *s-trans*-(*t*; θ = 180°), and *gauche*-forms (*g*; 0 < θ < 180°).

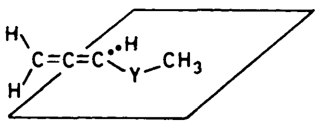
The p.e. spectrum of methoxyallene (**3**) was investigated by Runge *et al.*[8] assuming the existence of only one preferred conformation (*s-cis*). Later, Burgers *et al.*[9] performed an investigation of (**3**) and (**6**) with the aim to inquire into the existence of conformational equilibria for the ionic states of (**3**) and (**6**). They



(*c*)



(*g*)



(*t*)

interpreted the p.e. spectrum of (**3**), in particular, the lowest-energy p.e. band 1, as reflecting two conformers, **c** *versus* **t** with **c** being largely dominant. With reference to the p.e. band 1 of (**6**) it was assumed that the t-butoxy compound exists preferentially in the *s-trans* form.

It is our intention to inquire further into the problem of conformational equilibria of alkoxyallenes (**3**), (**5**), (**6**), but also of (alkylthio)allenes (**4**), (**7**), (**8**) utilizing p.e. spectroscopy.

There is considerable confusion about the conformational situation of (alkylthio)allenes. Burgers[9] inferred [from the p.e. spectrum of (**4**) in conjunction with semiempirical calculations] that for (**4**) only one conformer is present (whose geometry cannot deviate significantly from planarity). On the other hand, an electron diffraction study of (**4**)[10] suggested (**4**) to exist as a *cis-gauche* equilibrium. Finally, *ab initio* calculations predicted two stable conformers for (**4**)[11] one being the planar *s-cis* form. However, on the STO-3G level the second stable conformer was calculated to be *s-trans*, whereas on the 44-31G level a *gauche* form was found to be the second stable conformer.

The existence of *gauche* conformers has an important consequence for the electronic structures of the investigated allenes. In monosubstituted allenes of C_s symmetry [as are **c** and **t** of (**3**)—(**8**)] there is a strict separation of $\pi(a'')$ and $\sigma(a'')$ orbitals.[8,12,13] Generally, the outermost σ orbitals are denoted as $\bar{\pi}$ ('perpendicular π orbitals').[8,12,13] In allenes with gauche conformations, however, the lack of spatial symmetry lifts the π–$\sigma(\bar{\pi})$-separation of MOs and the close lying orbitals $\pi_{(1)}$ and $\bar{\pi}_{(1)}$ (and $\bar{\pi}_{(1)}{}^*$ and $\bar{\pi}_{(1)}{}^*$) may mix. Then, it is no longer possible to interpret substituent effects in terms of separated π- and σ-interactions.[8]

The above considerations on the breakdown of the π–σ-separation are especially important for (dimethylamino)allene (**2**), if the amino group has a pyramidal structure or, with a (locally) planar amino group, a gauche conformation [*g*; Y = $N(CH_3)$] contributes significantly to the conformer population. In order to inquire into the molecular structure of (**2**) a geometry optimization was performed on the semiempirical MINDO/3 level.

Experimental

t-Butylallene (**1**) was obtained by the procedure given in ref. 14. All the other compounds (**2**)—(**8**) were synthesized by isomerization of correspondingly substituted acetylenes $HC{\equiv}CH_2Z$ according to standard procedures[15] [*cf.*, in particular, ref. 16 for (**2**), ref. 17 for (**3**), (**5**), (**6**), and ref. 18 for (**4**), (**7**), (**8**)].

The photoelectron spectra were run on a Vacuum ESCA-2 spectrometer at a resolution of 2 meV using He^{I} emission as the ionizing source. Calibration was done with Xe or Ar, respectively, as internal standards.

Semiempirical MINDO/3 calculations were performed according to common procedures.[19] Geometry optimization for (**2**) was done using the Davidon–Fletcher–Powell search routine.

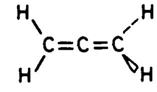
Table 1. Vertical ionization energies (I_v), vibrational spacings ($\tilde{\nu}^+$), and assignments for p.e. bands of allenes $XCH{=}C{=}CH_2$

Band	I_v/eV	$\tilde{\nu}^+$/cm^{-1} [a]	Assignment [b]
X = $C(CH_3)_3$ (**1**)			
1	9.32	1 600 1 370	$\pi_{(1)} \approx \pi_A(a'') - \pi_X(a'')$
2	9.70	1 600	$\bar{\pi}_{(1)} \approx \bar{\pi}_A(a') - \bar{\pi}_X(a')$
3	10.48 [c]	1 600 850	$\bar{\pi}_{(2)} \approx \bar{\pi}_X(a') + \bar{\pi}_A(a')$
4	11.68	800	$\pi_{(2)} \approx \pi_X(a'') + \pi_A(a'')$
X = $N(CH_3)_2$ (**2**)			
1	7.55 (7.78) [d]	550	$\pi_{(1)} \approx \pi_A(a'') - \pi_X(a'')$ [e]
2	9.64 (9.58) [d]	930	$\bar{\pi}_{(1)} \approx \bar{\pi}_A(a') - \sigma(C{-}NC_2)$
3	10.52 (10.59) [d]	650	$\pi_{(2)} \approx \pi_X(a'') + \pi_A(a'')$
4	12.51 (11.45) [d]		$\sigma(C{-}NC_2)$

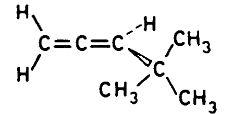
[a] Vibrational spacings may be in error by ± 100 cm^{-1}. [b] According to the LCMO model the MOs are composed of allenic (A) and substituent (X) orbitals of corresponding symmetry [where $\pi_A(a'')$ and $\bar{\pi}_A(a')$ correspond to a″ and a′, respectively, components of the allenic 2e orbital].[8,12,13] [c] Band centre. [d] MINDO/3 negative orbital energies. [e] $\pi_X(a'') \approx n_N$.

Results and Discussion

t-Butylallene and (Dimethylamino)allene.—Vertical ionization energies (I_v), vibrational spacings ($\tilde{\nu}^+$), and assignments for the low-energy p.e. bands with I_v < 12.5 eV of t-butylallene (**1**) and (dimethylamino)allene (**2**) are summarized in Table 1. The interpretation of the p.e. spectra is based on the LCMO model used in refs. 8 and 12 with the emphasis on the interactions between the outermost 2e orbital of allene (**9**) and the outermost π and σ orbitals of the substituents.

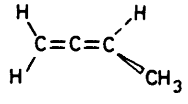


(**9**)



(**1a**)

For (**1**) it is reasonable to assume the preference of one conformer (**1a**) of symmetry C_s with a methyl group eclipsing the double bond.[13,20] In the lowest-energy region the shape of the p.e. spectrum of (**1**) with three peaks (9.32, 9.52, 9.70 eV) of almost equal intensity and vibrational progressions of 1 600 cm^{-1} is notable (Figure 1). The 1 600 cm^{-1} vibrational progression is also observed for other alkylallenes with C_s (or C_{2v}) symmetry, such as methylallene (**10**)[6] and can be attributed to the asymmetric C=C=C stretching mode ($\tilde{\nu}_{as}$ 1 960 cm^{-1} in the ground state of corresponding allenes).[13] In contrast to (**10**), however, where in the lowest-energy p.e. band the 0—0 transition is of highest intensity, (**1**) has the 0—3 (or 0—4) vibrational progression with the highest intensity.



(**10**)

$(CH_3)_3CH$

(**11**)

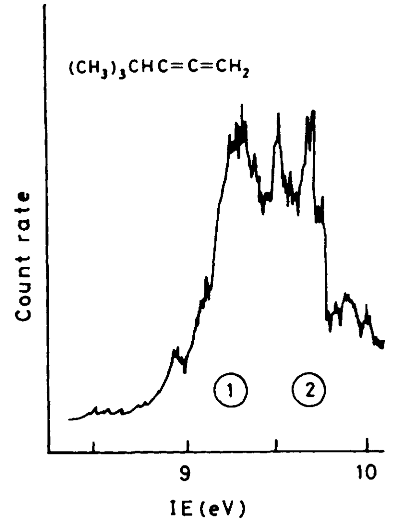


Figure 1. The lowest-energy He^I photoelectron spectral bands of t-butylallene (**1**)

The lowest-energy p.e. bands 1 and 2 can be related to ionizations of the outermost a″ ($\pi_{(1)}$) and a′ orbitals ($\bar{\pi}_{(1)}$).[8,12,13] In terms of a LCMO model[8,12] $\pi_{(1)}$ ($\bar{\pi}_{(1)}$) correspond to the antisymmetric combination of the a″ (a′) component of the allenic 2e orbital (π_A, $\bar{\pi}_A$; with energy −10.07 eV)[8] and the a″ (a′) component of the isobutane (**11**) outermost e orbital (π_X, $\bar{\pi}_X$; with energy −10.50 eV).[21]

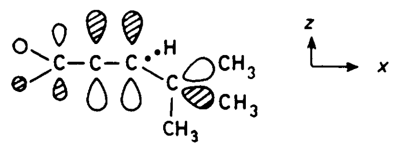
For energy reasons (referring to the split between π orbitals) ionization from the symmetric combination of the a″ (2e) orbital of (**9**) and the e(a″) group orbital of (**11**) must be associated with band 4 (11.68 eV) which exhibits 800 cm^{-1} vibrational progressions. This vibrational mode should correspond to the CH$_2$ torsional motion around the C=C=C axis, as is also found in the allene (**9**) radical cation.[5,6]

Band 3 must result from ionization of the second a′ orbital ($\bar{\pi}_{(2)}$) (symmetric combination of corresponding group orbitals). The involvement of the antisymmetric C=C=C stretching vibration in the ionization of $\bar{\pi}_{(2)}$ reveals that this orbital has considerable allenic character. The second progression of band 3 can be tentatively attributed to the C_{sp^2}–C_{sp^3} stretching vibration [found at 876 cm^{-1} in the ground state of (**10**)].[22]

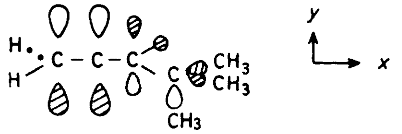
As in the LCMO model the extent of resonance interactions between two MOs is related directly to the overlap between the relevant orbitals and inversely proportional to the energy gap between them, the $\bar{\pi}$–σ interaction between the allenic orbital $\bar{\pi}_A$ (of energy −10.07 eV) and the t-butyl group orbital $\bar{\pi}_X$ (−10.50 eV) should be rather strong in (**1**). The particular forms of $\bar{\pi}_A$(a′) (composed of p_y AOs) and $\bar{\pi}_X$(a′) in conformation (**1a**) allow a π-type hyperconjugation which is visualized in (**B**). For comparison the schematic MO representation of $\pi_{(1)}$ of (**1**) is given in (**A**).

As noted in the Introduction the larger delocalizations of $\pi_{(1)}$ and $\bar{\pi}_{(1)}$ across the allenic skeleton in (**1**) than in (**10**) explain the absence of a pseudo-JT-effect in (**1**). This inference is further supported by the calculational model for (electronic) substituent effects on p.e. bands in 1,3-disubstituted allenes.[7,13]

Accordingly, theoretical ionization energies of (**1**) are: $I_v(\pi_{(1)})$ 9.30, $I_v(\bar{\pi}_{(1)})$ = 9.70 eV (in perfect agreement with experiment). This means that the shifts of the p.e. bands 1 and 2 relative to the 2e orbital energy of allene (**9**) result only (or overwhelmingly, respectively) from intrinsic electronic effects of the (CH$_3$)$_3$C group. The particular shape of the last p.e. bands probably results from accidental overlap of vibrational bands near 9.52 eV to give the resultant band an intensity comparable to those at 9.32 and 9.70 eV.



(A) ($\pi_{(1)}$)



(B) ($\bar{\pi}_{(1)}$)

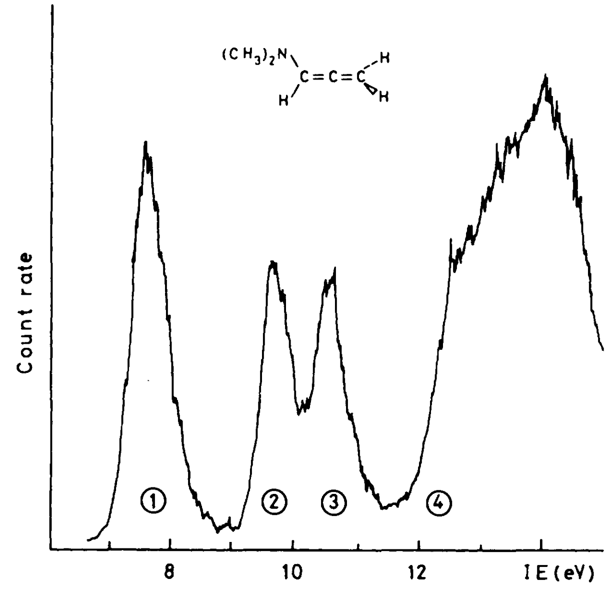


Figure 2. He^I photoelectron spectrum of (dimethylamino)allene (**2**)

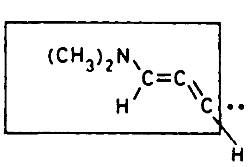
In Figure 2 the p.e. spectrum of (dimethylamino)allene (**2**) is displayed. The dimethylamino group is known to exert the largest of all the donor resonance effects ($\sigma_R{}^0$ −0.52,[23a] $\sigma_R{}^0$ − 0.55,[23b] $\sigma_R{}^+$ −1.75[23a]), but a rather small or medium, respectively, electric field effect [σ_I +0.06;[23a] group dipole moment $\mu(NMe_2)$ 1.6 D[24]]. As the allene moiety (HC=C=CH$_2$) represents also a moderately strong π donor,[12] the interaction of both these donor functionalities is of particular interest. Both moieties have close ionization energies for their HOMOs [$I_v(n_N)$ = 9.64 eV for HN(CH$_3$)$_2$].[25]

Band 1 evidently is associated with ionization from the π-HOMO [assuming a C_s symmetry for (**2**) as a first approximation]. Using the ionization energy of the π-HOMO of dimethylaminobenzene (7.51 eV)[26] correlation (2)[12] predicts $I_v(\pi_{(1)})$ 7.55 eV for (**2**), in agreement with the experimental value (Table 1).

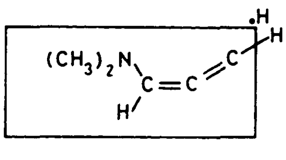
$$I_v(RCH{=}C{=}CH_2) = 1.33\, I_v(C_6H_5R) - 2.44 \qquad (2)$$

Band 1 is symmetrical and has marked vibrational progressions of 550 cm^{-1}, the vertical ionization being reached for the 0—4 (or 0—5) transition. This means that the ionized state of (**2**) suffers considerable geometrical deformations. We assign the observed vibrational progressions to bending modes of the

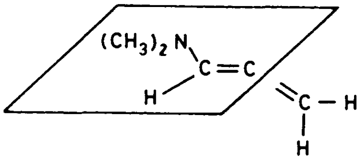
C=C=C skeleton. Such skeletal bending motions are also observed in the radical cations of t-butyl-halogenoallenes $(CH_3)_3CCH{=}C{=}CHX$ (X = Cl, Br).[7] For the halogenoallenes C=C=C bending has frequencies of $\tilde{\nu}(a'')$ 603 and $\tilde{\nu}(a')$ 519 cm^{-1} ($H_2C{=}C{=}CHBr$) in the neutral ground state.[13] Tentatively, we attribute the particular vibrational motion to bending-in-plane [bip; $\tilde{\nu}^+(a')$]. For steric reasons the vibrational motions should favour the *trans*-form (**2-*t***) over the *cis*-form (**2-*c***). In support of this suggestion one can argue as follows. Band 1 of (**2**) is found at the position expected from correlation (2). This correlation is based on comparisons of π-orbitals of molecules with mirror plane symmetries. Compound (**2-*t***) and also (**2-*c***) retain C_s symmetry. For bending-out-of-plane (bop), as in (**2a**), the mirror plane symmetry is lifted and one has a breakdown of the π–σ separation of MOs. In this last case the MOs $\pi_{(1)}$ and $\bar{\pi}_{(1)}$ should mix considerably and shift the ionization energy away from the value 7.55 eV. As vibrations excited in p.e. spectra usually correspond to motions of the atoms in that part of the molecule where the ionized electron is most heavily localized, the observation of the C=C=C bip indicates that the HOMO $\pi_{(1)}$ retains its allenic character to a large extent.



(**2-*t***)



(**2-*c***)



(**2a**)

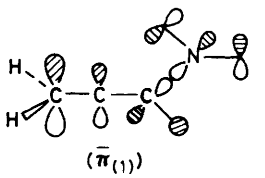
For energy reasons band 2 with an asymmetry to higher energy corresponds to ionization from the $\bar{\pi}_{(1)}$ orbital. It exhibits a 930 cm^{-1} vibrational progression. It can be attributed to the symmetric C=C=C stretch [$\tilde{\nu}_s$(C=C=C)] which is often found to be excited upon ionization of $\bar{\pi}_{(1)}$ of monosubstituted allenes.[8]

The third p.e. band of (**2**) should be associated with the second π orbital, $\pi_{(2)}$. The vibrational spacing of band 3 (650 cm^{-1}) is tentatively assigned to the CH_2 wagging occurring near 860 cm^{-1} in monosubstituted halogenoallenes.[27] Band 4 of (**2**) (at 12.51 eV) is the sharp onset of a broad system of overlapping bands. We attribute band 4 to ionization of the σ(C–NC_2) orbital. The corresponding band of dimethylamine is found at 12.70 eV.[25]

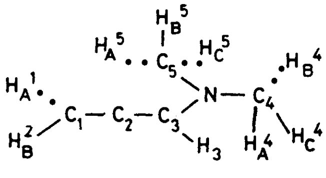
The MO $\bar{\pi}_{(1)}$ of (**2**) exhibits one of the most pronounced destabilizations observed for this type of orbital[8,12] in monosubstituted allenes. This is remarkable, as $\bar{\pi}_{(1)}$ is decisively influenced by Coulombic forces through space (induced by the groups' dipole moments).[8,12] From correlation (3) $\bar{\pi}_{(1)}$ of (**2**) is

$$I_v(\bar{\pi}_{(1)})(RCH{=}C{=}CH_2) = 10.07 + 0.25\,\mu(X) \qquad (3)$$

expected to have an orbital energy of −10.47 eV. The *ca.* 0.8 eV destablization of $\bar{\pi}_{(1)}$ relative to the expected value cannot be fully explained referring to $\bar{\pi}$–σ 'hyperconjugative' interactions, as observed for $\bar{\pi}_{(1)}$ in other allenes[7,8] and visualized by (**C**). The $\bar{\pi}$–σ hyperconjugation should account for no more than 0.3—0.5 eV destabilization.[8] We suggest that the preferred conformation of (**2**) has no mirror plane symmetry so that $\pi_{(1)}$ and $\bar{\pi}_{(1)}$ can mix and repel each other energetically. The conformational conjecture about the additional destabilization of $\bar{\pi}_{(1)}$ through π–π mixing is supported by semiempirical MINDO/3 calculations. Geometry optimization of (**2**) gives a structure (**2b**) lacking the C_s symmetry of other monosubstituted allenes.



(**C**)



(**2b**)

Bond distances (Å)

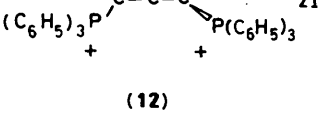
C(1)–H_A(1)	1.102	C(3)–N	1.389
C(3)–H(3)	1.119	N–C(4)	1.421
C(1)–C(2)	1.300	N–C(5)	1.421
C(2)–C(3)	1.323	C_{sp^3}–H	1.120

Bond and dihedral angles (°)

C(2)C(1)H_A(1)	124.80	C(5)NC(3)	122.52
C(3)C(2)C(1)	180.00	C(4)NC(3)	120.31
H(3)C(3)C(2)	115.97	C(4)NC(3)H(3)	−9.82
C(2)C(3)N	130.32	C(5)NC(3)H(3)	172.79

C(4) and C(5) are slightly twisted out of the plane defined by H(3), C(3), N, *i.e.* the nitrogen achieves a pyramidal arrangement. One methyl group of the $(CH_3)_2N$ moiety (almost) eclipses the double bond, as is a preferred conformation (**c**) of $H_2C{=}C{=}CHYCH_3$ molecules.[20] The four atoms H_B(2), H_A(1), H(3), and N are situated in exactly perpendicular planes. The allenic C=C=C axis is linear.

There exist no experimental structural data for (**2**). Hence, the theoretical data of (**2b**) (for the gas phase) must be compared with general structural features observed for allenes[20] and *X*-ray data for compound (**12**).[28] The bond lengths for the C=C bonds of (**2b**) agree with those generally found for monosubstituted allenes.[20] However, MINDO/3 makes the (substituted) C(2)– C(3) bond longer than C(1)–C(2) by 0.023 Å. For all the allenes studied so far[20] both the C=C bonds have equal lengths within 0.01 Å. The lengthening of the substituted double bond relative to the other one is probably due to an inherent deficiency of the MINDO/3 scheme. For instance, for cyclopropylallenes MINDO/3 also attributes to the substituted bond a length greater than the other C=C bond by 0.03 Å.[20] The theoretical C_{sp^2}–H bond lengths do not differ significantly from the experimental values (r_{C-H} 1.067—1.091 Å).[20] The C(3)–N and N–C(4)[C(5)] bond lengths compare favourably with those found for (**12**) (1.39 and 1.42 Å).[28] Owing to markedly different



(**12**)

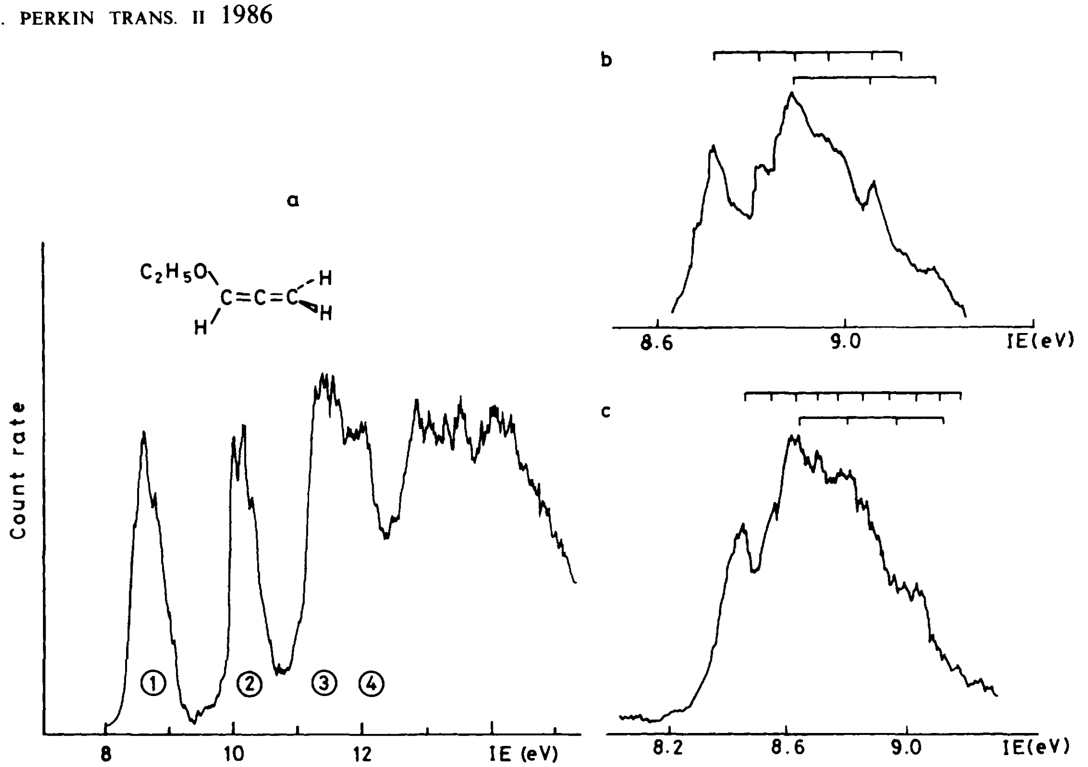


Figure 3. He^{1} photoelectron spectrum of ethoxyallene (**5**) (a) and comparisons of the higher resolved bands 1 of methoxyallene (**3**) (b) and **5** (c)

Table 2. Vertical ionization energies (I_v), vibrational spacings ($\tilde{\nu}^+$), and assignments of p.e. bands of alkoxyallenes $ROCH{=}C{=}CH_2$[a]

		R = CH_3 (**3**)[b,c]		R = C_2H_5 (**5**)[b]		R = $C(CH_3)_3$ (**6**)	
Band	Assignment[a]	I_v/eV	$\tilde{\nu}^+$/cm^{-1}	I_v/eV	$\tilde{\nu}^+$/cm^{-1}	I_v/eV	$\tilde{\nu}^+$/cm^{-1}
1	$\pi_{(1)} \approx \pi_A - \pi_X$	8.73 (8.75)	1 260 800	8.47	1 300 850	8.31	800
2	$\bar{\pi}_{(1)} \approx \bar{\pi}_A - \sigma(COC)$	10.28 (10.33)	1 300	10.12	1 290	9.83	1 450
3	$\sigma(COC)$	12.02 (12.0)		11.41	890	10.99	
4	$\pi_{(2)} \approx \pi_A + \pi_X$	12.34 (12.2)		12.08		12.19	

[a] For the accuracy of the vibrational spacings and the band assignment notation *cf.* footnotes *a* and *b* of Table 1. [b] *Cf.* text. [c] Values in parentheses are from ref. 8.

steric situations it is not meaningful to compare bond angles of (**2b**) and (**12**). However, it should be noted that in (**12**) the nitrogen atom achieves also a pyramidal arrangement with its attached groups. Furthermore, one methyl group of the $(CH_3)_2N$ moieties eclipses (almost) the double bonds, as predicted for (**2b**).

The MINDO/3 (negative) orbital energies for the four highest energy MOs of (**2**) are in very good agreement with the experimental ionization energies (Table 1). Based on structure (**2b**) the MINDO/3 calculations corroborate that the π and $\bar{\pi}$ MOs do not remain pure. In particular, the highest-energy MOs can be approximately described according to equation (4). In

$$\varphi_{(1)} \approx N_1[\pi_{(1)} - 0.1\,\bar{\pi}_{(1)}] \qquad (4a)$$

$$\bar{\varphi}_{(1)} \approx \bar{N}_1[\bar{\pi}_{(1)} + 0.1\,\pi_{(1)}] \qquad (4b)$$

equation (4) N_1 and $\bar{N}_1$, respectively, represent normalization constants.

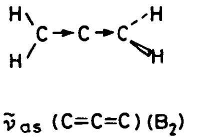
Alkoxyallenes.—In Table 2 vertical ionization energies, vibrational spacings, and assignments of the lowest energy p.e. bands of alkoxyallenes (**3**), (**5**), and (**6**) are given. In Figure 3 the p.e. spectrum of (**5**) is displayed. A p.e. band assignment of methoxyallene (**3**) on the basis of Koopmans' approximation was presented in ref. 8. It was supported by *ab initio* (STO-3G, STO-4.31G)[8] and semiempirical (CNDO/S,[8] MINDO/3,[9] MIEHM[9]) calculations. Owing to the relatively small perturbation of the corresponding orbitals when substituting CH_3 by the other alkyl groups [C_2H_5, $(CH_3)_3C$] the band assignments for the alkoxyallenes in Table 2 are straightforward (using energy arguments). The orbital notation is Table 2 is as usual.[8,12,13] In particular, $\pi_X(a'')$ corresponds to the oxygen lone-pair and σ(C–O–C) is essentially a C–O–C σ orbital which is continuously destabilized (by *ca.* 0.5 eV) substituting methyl (**3**) by ethyl (**5**) and t-butyl (**6**).

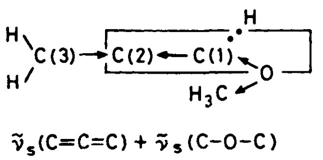
The vibrational structures of bands 1 and 2 of (**5**) and (**3**) are very similar and are given (with the emphasis on band 1) in Figure 3. This means that the corresponding subunits of the radical cations (**3**$^+$) and (**5**$^+$) have comparable degrees of freedom for nuclear motion and the geometrical situations for both species are comparable.

In band 1 of (**3**) and (**5**) at least two vibrational progressions are active, one with a frequency of *ca.* 1 300 cm^{-1} and the other with an initial spacing of 800 cm^{-1}. The last mode diminishes with increasing energy to *ca.* 400 cm^{-1} for (**3**$^+$) and to *ca.* 540 cm^{-1} for (**5**$^+$). The understanding of the vibrational structure of the bands 1 (and 2) is a prerequisite for tackling the question of the existence of one or several conformers of the radical cations of alkoxyallenes. In ref. 8 the p.e. spectrum of (**3**) was interpreted assuming the existence of only one preferred conformation (***c***), in agreement with i.r.[9] and electron diffraction (e.d.) studies [10] of the neutral molecule (**3**) in the gas phase.

On the other hand, for (**3**) the two prominent p.e. peaks of band 1 at 8.73 and 8.90 eV (Figure 3) were interpreted as being due to two different conformers, *viz. s-cis* (***c***) and *s-trans* (***t***).[9] Furthermore, in ref. 9 the 800 cm^{-1} vibrational progression was assigned to C=C=C bending of one conformer. The other (apparently) two progressions (1 260 and 560 cm^{-1}) were attributed to asymmetric C=C=C stretch and C=C=C bend of the second conformer.

Generally, inferences about conformational equilibria of radical cations from p.e. spectra are not without hazard.[29] In our view the interpretation of the shape of the p.e. spectrum (band 1) of (**3**) in terms of the existence of two conformers and the assignments of the vibrational modes in ref. 9 are unlikely for the following reasons. First, the reduction of the asymmetric stretch from $\tilde{\nu}_{as}$ 1 955 cm^{-1} in the neutral molecule (**3**) [13] to 1 260 cm^{-1} in cation (**3**$^+$) would be extremely large (as was also pointed out by Burgers [9]). If present in a p.e. band of an allene the reduction of $\tilde{\nu}_{as}$ amounts to 10—20% [6,30] [*cf.* also (**1**), Table 1]. It seems more likely to attribute the 1 260 cm^{-1} progression of band 1 of (**3**) to C–O–C stretching [$\tilde{\nu}$ 1 215, $\tilde{\nu}$ 1 055 cm^{-1} in (**3**)] [13] or the allenic symmetric C=C=C stretch ($\tilde{\nu}_s$ 1 105 cm^{-1}),[13] or both. The C–O–C stretch comprises two C–O vibrations [$\tilde{\nu}_{as}$(C$\rightarrow$O$\rightarrow$C); $\tilde{\nu}_s$(C$\rightarrow$O$\leftarrow$C)] and may couple strongly with the close lying symmetric C=C=C stretch. A 1 260 cm^{-1} progression is also observed in p.e. band 1 of methyl vinyl ether ($H_2C{=}CHOCH_3$) and has been assigned to C–O–C stretching.[31] Considering all this we propose that in the p.e. band 1 of (**3**) the symmetric C=C=C and C–O–C stretching vibrations are active. The HOMO $\pi_{(1)}$ of (**3**) [and (**5**)] is essentially localized at the C(2)=C(1)–O subunit and has a node between the allenic and the alkoxy moieties. Hence, in (**3**) [and (**5**)] the simultaneous operation of $\tilde{\nu}_s$(C=C=C) and $\tilde{\nu}_s$(C–O–C) may induce a vibrational situation for C(2)=C(1)–O which is qualitatively similar to that of allene (**9**). In (**9**) the π_z-component of the 2e HOMO has a node between the central and the terminal allenic carbon atoms and in the radical cation (**9**$^+$) the three-atom skeleton is affected by the B_2 antisymmetric stretch.[5,6]





The analogy with the situation in (**9**) leads quite naturally to the interpretation of the other vibrational modes found in the p.e. spectra of (**3**) and (**5**). In the general theory [5] nonadiabatic vibronic coupling effects in radical cations involve (at least) two vibrational modes, (at least) one stretching and a torsional mode. In the radical cation (**9**$^+$) vibronic coupling (JT-effect) involves the B_1 torsional mode of the terminal CH_2 group [$\tilde{\nu}$ 865 cm^{-1} in (**9**)] [32] and the antisymmetric (B_2) C=C=C stretch. The JT-effect of (**9**$^+$) can be understood as a vibronic coupling induced by the torsional mode which is tuned by the stretching vibration.[5] The co-operation of both these nuclear motions gives regular torsional progressions only for low energy. For higher energy an irregular structure appears.[5] In (**9**$^+$) initial torsional spacings decrease from 807 to 403 cm^{-1} (at the high-energy side of the band).[32] Similarly, we attribute the vibrational progressions of band 1 of (**3**) [(**5**)] which start with spacings of 800 (850) cm^{-1} and decrease to 400 (540) cm^{-1} to the CH_2 torsional mode. Using this interpretation of the vibrational shapes of the p.e. bands 1 of (**3**) and (**5**) (induced by stretching and torsional modes) there are no longer indications of (*s-cis*/*s-trans*) conformational equilibria for (**3**$^+$) and (**5**$^+$). Furthermore, the closely similar structures and shapes of the bands 1 suggest (**3**) and (**5**) to exist in the same preferred conformation, *viz. s-cis* (***c***).

In the bands 2 of (**3**) and (**5**) the vibrational spacings of 1 300 and 1 290 cm^{-1}, respectively, should be due to combined actions of symmetric C=C=C and C–O–C stretching modes. The 890 cm^{-1} progression of band 3 of (**5**) is tentatively assigned to the antisymmetric C–O–C stretch.

The lowest-energy p.e. band 1 of t-butoxyallene (**6**) exhibits a vibrational structure different from those found for (**3**) and (**5**).[9] Here, only one vibrational mode with a 800 cm^{-1} spacing is observed. This mode should be associated with the CH_2 torsional motion. This finding suggests that relative to (**3**) and (**5**) in (**6**) the conformational situation has changed. The bulkiness of the t-butyl group makes an *s-trans* form or one severely deformed from the *s-cis* form (*i.e.* a *gauche* form) the only plausible ones. A *gauche* conformer, however, should induce marked π–$\bar{\pi}$ mixing and, hence, should widen the gap between the orbitals $\pi_{(1)}$ and $\bar{\pi}_{(1)}$. This is not observed [the split Δ between the bands 1 and 2 changes insignificantly in the series (**3**), (**5**), (**6**) (1.55, 1.65, 1.52 eV)]. Therefore, we assume (**6**$^+$) to exist preferentially in the *s-trans* form. The inferences about the different conformational situations of (**3**), (**5**), (**6**) are supported by consideration of the energy differences between the π orbitals (bands 1 and 4). For (**3**) and (**5**) this difference amounts to 3.61 eV, but to 3.88 eV for (**6**).

A detailed inspection of the substituent effects on the $\bar{\pi}$ orbital energies provides further support for the above deductions. Here, apart from vibronic coupling of $\pi_{(1)}$ and $\bar{\pi}_{(1)}$, two effects must be considered. Firstly, the energy of $\bar{\pi}_{(1)}$ is affected by the RO group dipole moment (through space).[8,12] Secondly, one must consider 'hyperconjugative' $\bar{\pi}_{(1)}/\sigma$(COC) interactions. In the *s-cis* conformations of (**3**) and (**5**) the addition of the two =C–O and O–C bond dipoles gives a resulting group moment of *ca.* 1 D which makes an angle of *ca.* 40° with the C=C=C axis. The action of this group moment [*cf.* equation (3)] will stabilize $\bar{\pi}_{(1)}$ by *ca.* 0.25 eV, so that $\bar{\pi}_{(1)}$ has an energy of *ca.* -10.3 eV.[8,12] On the other hand, in a *s-trans* conformation the RO group dipole moment is almost perpendicular to the C=C=C axis. According to the model presented in refs. 8 and 12 such a dipole moment orientation cannot affect $\bar{\pi}_{(1)}$, *i.e.* $\bar{\pi}_{(1)}$ should have an energy of -10.07 eV. Now, taking the hyperconjugative $\bar{\pi}_{(1)}$–σ(COC) interactions into account, the rather large energy gap between $\bar{\pi}_{(1)}$ and σ(COC) in (**3**) suggests that here the hyperconjugation may be neglected. In (**5**) and (**6**) this gap is reduced and, in particular, for (**6**) a destabilization of $\bar{\pi}_{(1)}$ by *ca.* 0.2 eV [as found for (**1**) and (**2**)] can be anticipated. Hence, for an *s-trans* form (**6**) should have an orbital energy $\varepsilon(\bar{\pi}_{(1)})$ *ca.* -9.9 eV, as is observed experimentally.

Our conclusions from p.e. spectroscopy about the conformer situations of (**3**), (**5**), (**6**) in the gas phase find their counterparts in solutions. From n.m.r. spectroscopy it was deduced that (**3**) and (**5**) exist preferentially as the *s-cis* conformers, whereas for (**6**) the *s-trans* form dominates.[33a] Furthermore, the different conformational situations of (**3**), (**5**), (**6**) are also reflected by

Table 3. Comparisons between measured vertical ionization energies (I_v) and calculated orbital energies (ε_i) of *s-cis*-(methylthio)allene (**4**)

			$-\varepsilon_i$ (eV)			
Band	Orbital	I_v/eV[a]	MIEHM[a]	MINDO/3[a]	CNDO/S[c]	STO-3G
1	$\pi_{(1)}(a'')$	8.24[a,b]	10.59	8.45	9.64 (9.60)	6.22
2	$\bar{\pi}_{(1)}(a')$	9.86[d]	11.78	9.28	10.06 (10.06)	8.08
3	$\pi_{(2)}(a'')$	10.85	12.44	10.70	12.20 (12.11)	9.75
4	σ(CSC)	11.72	12.31	10.24	13.11 (12.66)	9.81

[a] From ref. 9. [b] vibrational progressions $\tilde{\nu}^+$ 600 cm^{-1}. [c] Including sulphur 3*d* AOs, values in parentheses are calculated without S 3*d* AOs. [d] Vibrational spacing $\tilde{\nu}^+$ 1 300 cm^{-1}.

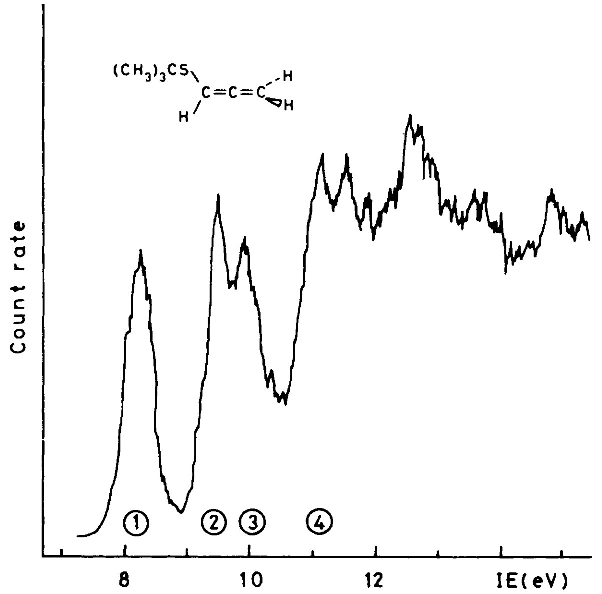


Figure 4. He^I photoelectron spectrum of (t-butylthio)allene (**8**)

chemical reactivity. Compounds (**3**) and (**5**) are metallated with LiN$(C_2H_5)_2$ at C(1), whereas (**6**) is metallated at the unsubstituted carbon [C(3)].[33b]

(*Alkylthio*)*allenes*.—The p.e. spectrum of (methylthio)allene (**4**) is displayed in ref. 9. Its ionization energies are summarized in Table 3. The suggested assignment of bands 1—4 was assumed to be supported by semiempirical MINDO/3 and MIEHM calculations (Table 3).[9] In particular, band 3 (10.85 eV) was attributed to ionization from the sulphur in-plane lone-pair $n_y^S(a')$ and band 4 (11.72 eV) to ionization of the second π orbital [$\pi_{(2)}(a'')$].[9] In terms of an LCMO model the n_y^S orbital is better described as a $\sigma(SCH_3)$ orbital and its interaction with $\bar{\pi}_{(1)}$ will lead to a σ(CSC) orbital. If the assignment of Burgers[9] were correct, the split Δ_π between the orbitals $\pi_{(1)}$ and $\pi_{(2)}$ of (**4**) (reflecting resonance interactions between the allenic and the substituent π orbitals) would amount to 3.48 eV. Hence, Δ_π would be much larger than that of (**2**) (2.97 eV; Table 1) and comparable with that of (**3**) (3.61 eV; Table 2), both these last compounds having very strong π donors. Therefore, we feel the assignment of Burgers[9] to be unlikely. Furthermore, in relation to the above semiempirical calculations the CNDO/S scheme reverses the sequence of the orbitals σ(CSC) and $\pi_{(2)}$. If sulphur *d*-AOs are included, the CNDO/S scheme predicts a gap of 0.91 eV between the bands 3 and 4, in agreement with the experiment. The same sequence as on the CNDO/S level is found by *ab initio* STO-3G calculations (Table 3). However, as the theoretical values for σ(CSC) and $\pi_{(2)}$ differ only little, the band assignment using the STO-3G results is not reliable.

On the other hand, using the ionization energy $\varepsilon(\pi_{(2)})$ -11.0 eV for (methylthio)ethylene ($CH_3SCH{=}CH_2$)[34] the correlation given in ref. 12 predicts the corresponding allene (**4**) to have an ionization energy $I_v(\pi_{(2)})$ 10.92 eV. Finally, with the simple LCMO model and the (non-optimized) parameters given in ref. 8 one obtains $\varepsilon(\pi_{(1)})$ -8.45, $\varepsilon(\pi_{(2)})$ -11.16, $\varepsilon(\pi_{(3)})$ -14.80 eV. This gives a theoretical split of 2.71 eV between $\pi_{(1)}$ and $\pi_{(2)}$, in agreement with the experiment, if band 3 is related to ionization of $\pi_{(2)}$.

All the above evidence shows that band 3 of (**4**) corresponds to the second π orbital and band 4 to the ionization of σ(CSC).

With regard to the close electronic and steric characteristics of the methyl and ethyl groups the p.e. band assignment for (**4**) should also hold for (ethylthio)allene (**7**) (Table 4). All the p.e. bands of (**7**) have slightly lower ionization energies than the corresponding ones of (**4**). In particular, for (**4**) and (**7**) the orbitals σ(CSC) have ionization energies which differ by no more than -0.36 eV from the energies of the second p.e. bands [attributed to $\sigma(SCH_3)$] of mercaptans RSH (R = CH_3, C_2H_5).[35] Furthermore, the shapes of the p.e. band 1 of (**4**)[9] and (**7**) are very similar. They are relatively sharp, but asymmetric with the 0—0 (or 0—1) transitions being the most intense vibrational components. For the ethers (**3**) and (**5**) the maxima are at higher vibrational members. This indicates a lesser change of geometry upon ionization of the HOMOs of the sulphur compounds. The regular 600 cm^{-1} progression of p.e. band 1 of (**4**$^+$) (Table 3) is attributed to one of the (symmetric or antisymmetric) C–S–C stretching modes [found at $\tilde{\nu}$ 754, 695 cm^{-1} in (**4**)].[13] The corresponding vibrational mode is also observed for band 1 of (**7**$^+$). In this regard the sulphides (**4**) and (**7**) are similar to the ethers (**3**) and (**5**), where in p.e. band 1 the C–O–C stretch is operative. Both bands 2 and 3 of (**7**$^+$) have *ca.* 1 300 cm^{-1} progressions which are also found for band 2 of the ethers (**3**) and (**5**). As, owing to the different energy gaps between the involved vibrations, mixing of $\tilde{\nu}_s$(C=C=C) and $\tilde{\nu}$(C–X–C) is less effective for X = S than for X = O, the observed 1 300 cm^{-1} progressions may also correspond to =C–H bending in-plane.[7]

The close correspondence of the p.e. spectra of (**4**) and (**7**) suggest that for both compounds similar conformational situations exist. The sharp p.e. band 1 of (**4**) and (**7**) do not indicate the presence of more than one conformer. By analogy with (**3**) and (**5**) we assume this to be the *s-cis* form which is calculated to be the preferred form for (**4**).[11]

The situation is more complex for the t-butyl compound (**8**) whose p.e. spectrum is given in Figure 4. Most remarkably, p.e.

Table 4. Vertical ionization energies (I_v), vibrational spacings ($\tilde{v}^+$), and p.e. band assignments for (alkylthio)allenes RSCH=C=CH$_2$

	R = C_2H_5 (**7**)			R = $C(CH_3)_3$ (**8**)		
Assignment	Band	I_v/eV	$\tilde{v}^+$/cm^{-1}	Band	I_v/eV	$\tilde{v}^+$/cm^{-1}
$\pi_{(1)} = \pi_A(a'') - \pi_X(a'')$	1	8.09	750	1	8.26	850, 450 1 050
$\bar{\pi}_{(1)} = \bar{\pi}_A(a') - \sigma(CH_3S)$	2	9.72	1 300	2	9.56	
$\pi_{(2)} = \pi_A(a'') + \pi_X(a'')$	3	10.64	1 290	4	11.21	1 770
$\sigma(CSC) = \sigma(CH_3S) + \bar{\pi}_A(a')$	4	11.30		3	10.00	1 290

band 1 of (**8**) is rather symmetric with the 0—3 (or 0—4) vibrational transition being the most intense one. Hence, the radical cation (**8**$^+$) exhibits a geometry which deviates considerably from that of the neutral molecule. Band 1 shows three different vibrational progressions (Table 4). They can be attributed to the symmetric C=C=C stretch ($\tilde{v}^+$ 1 050 cm^{-1}), a C–S stretching mode ($\tilde{v}^+$ 850 cm^{-1}), probably coupled with $\tilde{v}_s$(C=C=C), and a C=C=C bending vibration ($\tilde{v}^+$ 450 cm^{-1}) which is also active in the ionization of the π HOMO of (**2**) (Table 1). The C=C=C bending probably corresponds to the bip mode retaining the mirror plane symmetry of (**8**$^+$). As for (**2**$^+$), also for (**8**$^+$), the *trans* form should be preferred [*cf.* (**2**-*t*)].

With regard to the p.e. band assignment it is to be noted that band 4 of (**8**$^+$) has a 1 770 cm^{-1} vibrational progression. This mode is also operative in the ionization of the π HOMO of (**1**) and corresponds to the asymmetric C=C=C stretch. We take this as an indication that band 4 of (**8**) results from ionization of a π orbital ($\pi_{(2)}$), in contrast to the situation for (**4**) and (**7**). This is supported by the fact that for this assignment the splits between the π orbitals ($\Delta_\pi = \pi_{(2)} - \pi_{(1)}$) in the sulphur compounds (**4**), (**7**), (**8**) are consistently smaller than Δ_π of the corresponding ethers (**3**), (**5**), (**6**) by 1.0 ± 0.1 eV.

The a′ HOMO ($\bar{\pi}_{(1)}$) of (**8**) is markedly destabilized, even more than that of (**2**). This should be due to an increased $\bar{\pi}$–σ(CSC) hyperconjugation relative to that found for (**4**). This strong interaction is also reflected by the energy position of the σ(CSC) orbital at 10.00 eV (the split between σ and $\bar{\pi}_{(1)}$ being only 0.44 eV). The corresponding orbitals in (**4**) and (**7**) have ionization energies which are larger by (at least) 1.3 eV.

The shape of p.e. band 1 of (**8**$^+$) which is different from those of (**4**$^+$) and (**7**$^+$) indicates that (**8**$^+$) on the one hand and (**4**$^+$), (**7**$^+$) on the other hand have different conformational situations. This is supported by the split between the π orbital in (**8**) (Δ_π 2.95 eV) which is different from the splits of (**4**) and (**7**) (2.61, 2.55 eV). Following the lines of arguments put forward for the alkoxyallenes we assume that (**8**$^+$) has a preferred conformation which is significantly different from those of (**4**$^+$) and (**7**$^+$), namely *s-trans* [as has (**6**)]. This finding for the radical cations of (alkylthio)allenes is at variance with that for the neutral molecules (**4**), (**7**), and (**8**) in solution. From n.m.r. experiments it was concluded that all the sulphides have the preferred *s-cis* conformation.[33a]

Acknowledgements

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