0.5.[6] In the absence of oxygen Turro et al.[10] found also δ = 0.98, but employing a considerably more complex integrated rate expression. Besides the convenience of analyzing the effect of the induced decomposition directly on the observed rate constant k (eq 5), the significant conclusion is that δ is independent of the lifetime of the sensitizer, namely triplet acetone. In other words, irrespective of the presence or absence of the triplet quencher oxygen, every induced decomposition encounter (step k_6) conserves the number of triplet acetone sensitizers by destroying a TMD molecule. Thus, these results imply that the postulated[4,18] TMD·^{3}A* complex is independent of the unquenched or oxygen quenched acetone triplet lifetime.

In degassed solutions it was established that $kq\ \tau_T$ = 1000 M^{-1} (50% error limit),[10] while in aerated solutions we found $\beta' k_6 \tau_5 = 0.78\ M^{-1}$ (17% error limit) for the TMD decomposition. If it is assumed that this difference is due solely to oxygen quenching effect, a long triplet state lifetime of acetone in benzene solution results. Using $\beta' = 0.5$ (determined by Turro and Lechtken[6]) and $\tau_5 \simeq 10^{-7}$ sec (suggested by Turro et al.[7]), we estimate that the natural lifetime of acetone triplets falls in the range $10^{-4} < \tau_T < 10^{-5}$ sec. This is in accord with acetone triplet lifetimes reported in acetonitrile solution[19] and in the gas phase;[20] however, these values are in serious disagreement with the value of 3×10^{-8} sec extrapolated from benzene quenching data.[21] Resolution of this discrepancy must await further work, either using photophysical measurements or photosensitized reactions of acetone in benzene solution.

In conclusion, the present method of determining the absolute emission intensities and rate constants is direct, simple, and convenient for studying the mechanism of chemiluminescent reactions. Reliable and useful data on singlet efficiencies, induced decomposition efficiencies, activation parameters, and lifetimes of excited states can be acquired by this method. Of particular advantage is the large concentration range dependence (ca. 10^5) that can be assessed for the emission intensities and rate constants, providing a high level of confidence in the mechanistic interpretations. As was illustrated for α-peroxylactone decarboxylations,[14] this method is useful for studying enhanced chemiluminescence intensities, permitting determination of triplet yields (β) Such a study is presently under way for TMD.[22]

Acknowledgment. Financial support of this work by the National Science Foundation is gratefully appreciated. We thank Professor J. W. Hastings for a Mitchell-Hastings photometer, as well as calibrating one of our "POPOP" cocktails.

References and Notes

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(2) On study leave from the Department of Chemistry, Catholic University of Valparaiso, Chile.
(3) Puerto Rico Nuclear Center. This paper was prepared in connection with work under contract No. AT-(40-1)-1833 with the U.S. Atomic Energy Commission.
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Photoelectron Spectra of Open Chain C_6H_6 Isomers

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Contribution from the Institut für Organische Chemie der Technischen Hochschule Darmstadt, D-61 Darmstadt, Germany, and the Institut für Organische Chemie der Universität Karlsruhe, D-75 Karlsruhe, Germany. *Received February 5, 1975*

Abstract: The He I photoelectron spectra of 1,2,4,5-hexatetraene (biallenyl, **1**), 3-methyl-1,2,4,5-hexatetraene (3-methylbiallenyl, **2**), 1,2,4-pentatriene (vinylallene, **3**), 1,2-hexadiene-5-yne (propargylallene, **4**), and 1,5-hexadiyne (bipropargyl, **5**) are presented. The assignments of the photoelectron bands are discussed in terms of ZDO molecular orbital models as well as of semiempirical calculations. It is shown that (i) the first four bands of the photoelectron spectra of **1**, **2**, **4** and **5** and the first three bands of the photoelectron spectra of **3** are due to the ionization out of a π-orbital and (ii) that interaction between the C–C bond connecting the olefinic moieties and the corresponding π-orbitals is important.

The electronic structure of conjugated and cumulated double bonds has been subject to many investigations by experimental as well as theoretical chemists.[3] We would like to add some further information on this theme by reporting the photoelectron (PE) spectra of 1,2,4,5-hexatetraene (biallenyl, **1**), 3-methyl-1,2,4,5-hexatetraene (3-methylbiallyl, **2**), 1,2,4-pentatriene (vinylallene, **3**), 1,2-hexadiene-5-yne (propargylallene, **4**), and 1,5-hexadiyne (bipropargyl, **5**).

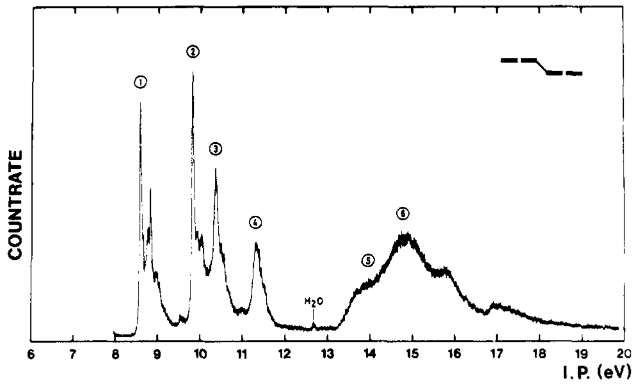
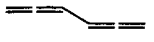
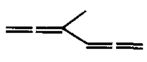


Figure 1. PE spectrum of 1,2,4,5-hexatetraene (biallenyl, **1**).



1



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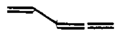

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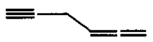

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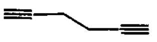
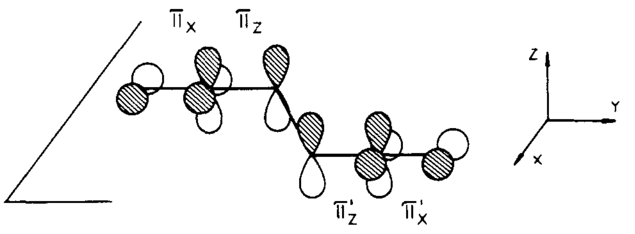
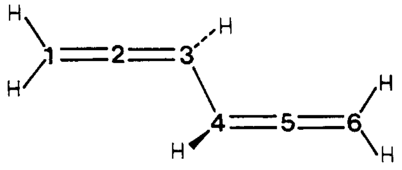


5

1,2,4,5-Hexatetraene (Biallenyl, 1)

Biallenyl[4] is the parent compound of two cumulated systems linked together by one carbon–carbon single bond. We will interpret its spectrum shown in Figure 1 using simple perturbation arguments[5] and the data gained by investigations of the remaining spectra to corroborate the results. Biallenyl is known to have C_{2h} symmetry.[6] It therefore contains two pairs of symmetry equivalent double bonds to which we shall refer as "inner" (π_z, π_z') or "outer" (π_x, π_x') double bonds. The conventional axes are shown below.





The π_z orbitals are conjugated and form a *transoid* butadiene system, while the π_x orbitals are separated by three carbon–carbon bonds.

Within C_{2h} symmetry one can write four symmetry adapted linear combinations that transform according to the following irreducible representations:

$$
\begin{aligned}
\Psi_1 &= (1/\sqrt{2})(\pi_z + \pi_z') \quad A_u \\
\Psi_2 &= (1/\sqrt{2})(\pi_z - \pi_z') \quad B_g \\
\Psi_3 &= (1/\sqrt{2})(\pi_x + \pi_x') \quad B_u \\
\Psi_4 &= (1/\sqrt{2})(\pi_x - \pi_x') \quad A_g
\end{aligned}
\qquad (1)
$$

Although this most common notation is simple and gives the main features of the expected π-orbitals, it does not account for any σ–π interaction, which will be shown to be of considerable importance. While the σ-counterparts of Ψ_1 and Ψ_2 must be "located" at the terminal methylene groups, the most important probable σ-contributors of Ψ_3 and Ψ_4 are "located" in the C–C framework. Semiempirical calculations agree with the expectation that a considerable through-bond interaction shifts ϵ_4 to lower values, while ϵ_3 rests practically unaffected.

Table I. Comparison between Measured Vertical Ionization Potentials, $I_{V,J}$, and Calculated Orbital Energies for **1** (all values in eV)

			Koopmans values			
Band	Orbital	$I_{V,J}$	CNDO/2	EH	MINDO/3	SPINDO
1	$b_g(\Psi_2,\pi)$	8.53	11.19	12.17	8.41	8.90
2	$a_g(\Psi_4,\pi)$	9.78	13.08	12.70	9.24	9.73
3	$b_u(\Psi_3,\pi)$	10.32	14.88	13.07	9.96	10.22
4	$a_u(\Psi_1,\pi)$	11.26	16.90	13.79	11.06	10.92
5	$a_g(\sigma)$	13.83	16.64	13.90	11.50	13.30

As a second-order effect, this σ–π mixing should be much smaller than the direct coupling of π_z with π_z'. The two occupied π-orbitals associated with conjugated double bonds are known to be split by more than 2 eV.[7]

As outlined above, it is expected that the orbital energies corresponding to Ψ_1 and Ψ_2, ϵ_1 and ϵ_2, are very different due to direct conjugation, while Ψ_3 and Ψ_4 are nearly degenerate. In other words:

$$\epsilon_1 \ll \epsilon_3 \approx \epsilon_4 \ll \epsilon_2 \qquad (2)$$

To proceed with the analysis of the spectrum of **1**, we now estimate the basis orbital energies $\langle \pi_x | H | \pi_x \rangle$ and $\langle \pi_z | H | \pi_z \rangle$, respectively.

Allene, in which both π orbitals π_z and π_x are degenerate by symmetry, shows one broad band with two distinct maxima at 10.07 and 10.64 eV, respectively, in its PE spectrum.[8,9] This bandshape has been ascribed to a Jahn–Teller distortion of the generated cation.[9,10]

By making the usual assumption of a symmetrical Jahn–Teller split,[11] one derives therefore basis orbital energies of

$$\epsilon(\pi_x) = \epsilon(\pi_z) = -10.35 \text{ eV} \qquad (3)$$

These estimated orbital energies have to be corrected for several terms. It is known, that the center of gravity of the two occupied π levels associated with two conjugated double bonds is shifted by approximately 0.3 eV toward higher energies with respect to the corresponding monoene.[12]

The orbital energy derived in eq 3 is "observed" in band 3 of the PE spectrum, while band 2 is shifted by 0.54 eV experiment, since the measured center of gravity of the two ionization potentials is ½(8.53 + 11.26) = 9.9 eV (see Table II). The two π_z orbitals are expected to split into Ψ_1 and Ψ_2 with an interaction element similar in magnitude as for *trans*-butadiene:

$$B(\pi_z) = \langle \pi_z | H | \pi_z' \rangle \approx 1.3 \text{ eV}^{13}$$

This yields $\epsilon_1 = -11.3$ eV and $\epsilon_2 = -8.7$ eV in perfect agreement with experiment.

The orbital energy derived in eq 3 is "observed" in band 3 of the PE spectrum, while band 2 is shifted by 0.54 eV toward higher energies. As mentioned above, this shift can be understood in terms of through-bond coupling.[14] The magnitude of this effect is in line with our observations made in *syn*- and *anti*-tricyclo[4.2.0.0^{2,5}]octadiene.[15] The orbital assignment therefore is quite unambiguously met and corroborated by semiempirical calculations of extended Hückel,[16] CNDO/2,[17] MINDO/3,[18] and SPINDO[19] type. The calculated Koopmans values are summarized in Table I and compared with the experimental ionization potentials. No method except for CNDO/2 predicts any other orbital being in the same range as the π-orbitals defined in eq 1. The CNDO/2 method also fails in predicting any reasonable splits between the levels associated with the inner ($\Delta\pi_z$) and the outer ($\Delta\pi_x$) double bond π-orbitals (see Table II).

Table II. Comparison between Experiment and Calculation for the Mean Ionization Potentials, $\bar{I}_p$, and the Splits $\Delta\pi$ Associated with the "Inner" (π_z and π_z') and Outer (π_x and π_x') π-Orbitals for **1**

		Calculation			
	Experiment	CNDO/2	EH	MINDO/3	SPINDO
$\bar{I}_{p(\pi_z)}$	9.89	14.04	12.98	9.74	9.91
$\bar{I}_{p(\pi_x)}$	10.05	13.98	12.88	9.60	9.97
$\Delta\pi_z$	2.73	5.71	1.62	2.65	2.02
$\Delta\pi_x$	0.54	1.81	0.37	0.71	0.49

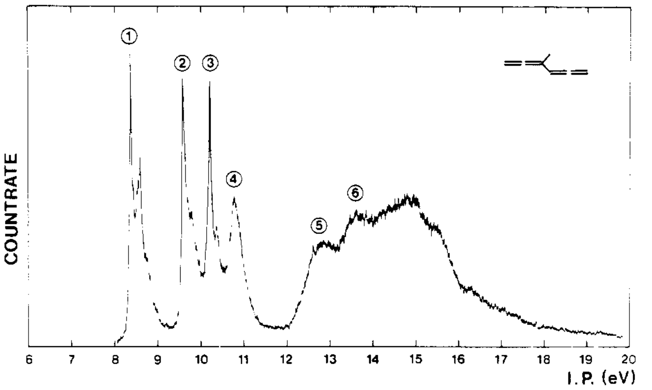


Figure 2. PE spectrum of 3-methyl-1,2,4,5-hexatetraene (3-methylbiallenyl, **2**).

Furthermore, the assignment is in full agreement with the one for 2,7-dimethyl-2,3,5,6-octatetraene discussed by Heilbronner et al.[9] It is interesting to note that in **1** the highest occupied σ orbital (a_g) is well below all π orbitals due to a strong σ–π interaction. In butadiene, where this σ–π interaction is missing, $\sigma(a_g)$ is nearly degenerate with $\pi(a_u)$.[13]

3-Methyl-1,2,4,5-hexatetraene (3-Methylbiallenyl, 2)

The 3-methyl derivative of **1** yields a PE spectrum (see Figure 2) that is easily explained using the available data of the appropriate comparable systems. The inner π-orbitals of **2** form a 2-methylbutadiene while in a first-order approximation, the outer π-orbitals are not affected by the methyl substitution (see Table III). This can be seen from Figure 3 where we have correlated the first bands of the PE spectra of **1** and **2**. The effect of methyl substitution of butadiene has been discussed in detail by Heilbronner et al.[20] using a LCBO model. A comparison of the experimental ionization potentials observed for 2-methylbutadiene with butadiene shows that ϵ_1 is shifted by

$$\Delta\epsilon_1 = -10.9 - (-11.46) = 0.56 \text{ eV}$$

while the HOMO is shifted by a much smaller amount of

$$\Delta\epsilon_2 = -8.89 - (-9.03) = 0.14 \text{ eV}$$

The discrepancy of the LCBO model in which both shifts should be equal has been explained in terms of through space interaction of the pseudo π-orbital of the methyl group with the nonsubstituted double bond.[20] The most naive treatment, however, yields an equivalent effect. In simple HMO theory, it is commonly assumed, that methyl substitution raises the "α-value" of the adjacent carbon atom.[21] Comparing ethylene with propylene yields a $\delta\alpha$ value of ($\delta\epsilon = c_i^2\delta\alpha$, $\delta\alpha = \delta\epsilon/c_i^2$):

$$\delta\alpha(\mathrm{CH_2{=}CH_2}) = 2(10.51 - 9.73) = 1.56 \text{ eV}$$

Applying this value and the common Hückel coefficients to butadiene one obtains

Table III. Vertical Ionization Potentials $I_{v,J}$ for **3** (all values in eV)

Band	Orbital	$I_{v,J}$
1	a″(π)	8.39
2	a′(π)	9.59
3	a′(π)	10.23
4	a″(π)	10.79
5	a′(σ)	12.62

Table IV. Comparison between Measured Vertical Ionization Potentials, $I_{v,J}$, and Calculated Orbital Energies for **3** Using the EH Method (all values in eV)

Band	Orbital	$I_{v,J}$	$-\epsilon_J$[EH]
1	a″(Ψ_2,π)	8.88	12.35
2	a′(Ψ_3,π)	10.04	12.80
3	a″(Ψ_1,π)	11.37	13.93
4	a′(σ)	12.55	13.80
5	a′(σ)	13.90	14.57

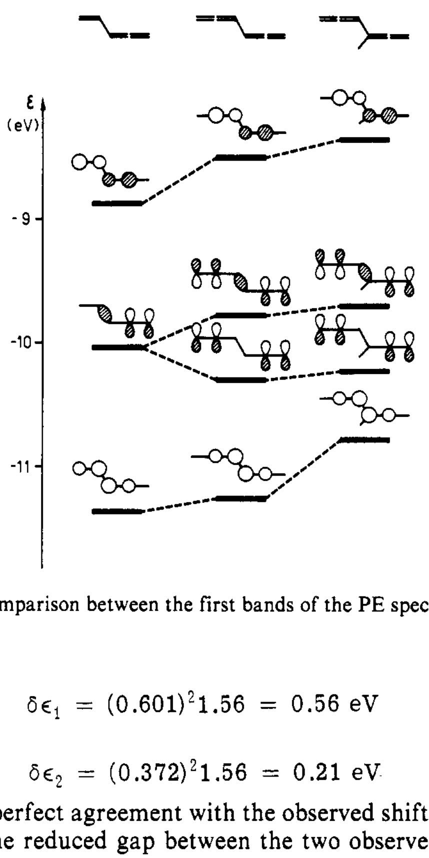


Figure 3. Comparison between the first bands of the PE spectra of **1**, **2**, and **3**.

$$\delta\epsilon_1 = (0.601)^2 1.56 = 0.56 \text{ eV}$$

and

$$\delta\epsilon_2 = (0.372)^2 1.56 = 0.21 \text{ eV}$$

in almost perfect agreement with the observed shifts and explaining the reduced gap between the two observed ionization potentials $I_{v,1}$ and $I_{v,4}$ in the spectrum of 2-methylbutadiene. It is also readily seen, that this model also fits the rules observed by Heilbronner concerning alkylated conjugated double bonds.[20]

Resuming the analysis of the PE spectrum of **2**, we therefore expect

$$\epsilon_1 = -\mathrm{IP}_1 = -8.53 + 0.21 = -8.32 \ (8.39)$$

and

$$\epsilon_2 = -\mathrm{IP}_4 = -11.26 + 0.56 = -10.70 \ (10.79)$$

which have to be compared with the "experimental" values that are given in parentheses (see also Table IV).

In addition, the through bond interaction between π_x and π_x' is expected to be increased, since a rising of the C–C σ-orbital $a_g(\sigma)$ decreases the energy difference between $a_g(\pi)$ and $a_g(\sigma)$ thus increasing second-order mixing. This effect—though impossible to explain quantitatively—indeed is observed (compare Figure 3).

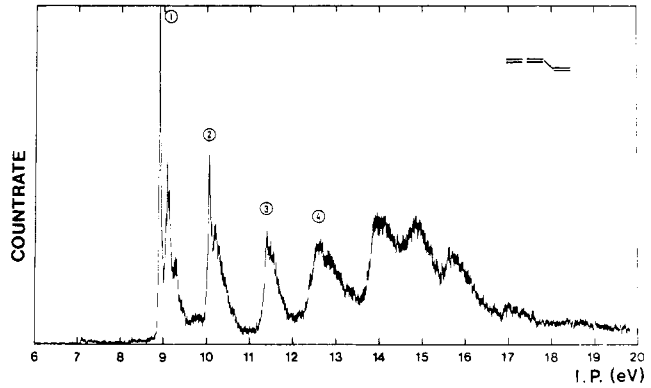


Figure 4. PE spectrum of 1,2,4-pentatriene (vinylallene, **3**).

At this point, we would like to emphasize that the LCAO-HMO-treatment reproduces the perturbations associated with methyl substitution while the LCBO model completely fails in predicting comparable ionization potentials.

1,2,4-Pentatriene (Vinylallene, 3)

The most stable ground state conformation of $\mathbf{3}^{22}$ has C_s symmetry;[23] i.e., *trans*-butadiene can serve as a model compound for this hydrocarbon. The PE spectrum of **3** is shown in Figure 4, and the data for the first five bands are presented in Table IV. In Figure 3 the PE spectra of **1** and **3** are compared.

Analogous to **1** we can define three symmetry adapted linear combinations

$$\Psi_1 = (1/\sqrt{2})(\pi_z + \pi_z') \quad A''$$
$$\Psi_2 = (1/\sqrt{2})(\pi_z - \pi_z') \quad A''$$
$$\Psi_3 = \pi_x \quad A'$$

Two of the π-orbitals, π_x, and π_z, are "allenic" π-orbitals ($\epsilon(\pi) \simeq -10.35$ eV, see eq 3) whereas the third one, π_z', is ethylenic ($\epsilon(\pi) = 10.56$ eV). Correction of both (π_z and π_z') basis orbital energies by the same "conjugative shift" of +0.3 eV and assuming the same resonance integral yields the following secular determinant

$$\left\|\begin{matrix} -10.21 - x & -1.3 \\ -1.3 & -10.05 - x \end{matrix}\right\| = 0$$

The calculated eigenvalues are $\epsilon_1 = -8.83$ and $\epsilon_2 = -11.43$ which again compare nicely with the experimental ionization potentials $I_{v,1}$ and $I_{v,3}$ (see Table IV).

Band 2 therefore has to be assigned to an ionization process in which an electron is ejected from the orbital π_x, e.g., the terminal allenic double bond. The somewhat lower value of 10.04 eV (expected within our model: 10.35 eV) can be explained by a stronger σ-π interaction of the C-C σ-bond with the terminal π-orbital than the σ-π interaction with the corresponding CH σ-bond in allene.

1,2-Hexadiene-5-yne (Propargylallene, 4) and 1,5-Hexadiyne (Bipropargyl, 5)

Unlike **1** to **3**, propargylallene (**4**) and bipropargyl (**5**) are expected to have one axis of nearly free internal rotation around the central carbon-carbon single bond. We have calculated the energies of the two molecules as a function of the rotational angle θ. The calculations were carried out within the EH approximation, a model which is known to give reasonable rotational barriers.[24]

The calculation shows, that the two molecules differ considerably with respect to internal rotation. For **4** the most stable rotamer was found to be in a gauche conformation, the dihedral angle θ being $\approx 70°$. The rotational barrier for this molecule was calculated to be 2.8 kcal/mol. This result suggests that all rotamers contribute to the PE spectrum with comparable intensities.

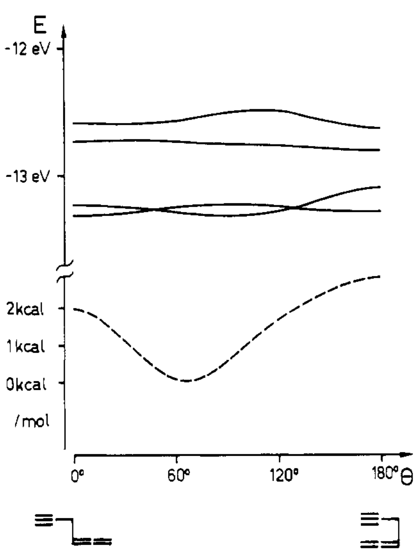


Figure 5. Highest four occupied MO's of **4** as a function of θ (top) and total energy of **4** as function of θ (bottom) according to an EH calculation.

We therefore examined how the orbitals shift as a function of the dihedral angle θ; the result of the EH calculation is illustrated in Figure 5.

It is readily seen, that the energies of the four relevant π-orbitals do not change significantly. This is expected, since for geometrical reasons through space interactions are absent, while the through bond mixing should be nearly independent of θ (the linking C-C σ-orbital in a localized picture is rotationally symmetrical around the axis, thus being nearly invariant to rotation). In contrast to this result, **5** has a high rotational barrier of more than 10 kcal/mol, the conformation of lowest energy having a planar, *transoid* conformation of the carbon skeleton ($\theta = 0°$). The PE spectra of **4** and **5** are shown in Figure 6 and compared in Figure 7. The relevant experimental data are collected in Table V. For the reason outlined above, we shall feel free to discuss the two spectra using the same conformations of the carbon framework: a *transoid*, planar configuration. In this conformation, the π-orbitals for **4** and **5** are given by the following equations:[25]

4	5
$\pi_x = (1/\sqrt{2})(p_{x1} + p_{x2})$	$\pi_x = (1/\sqrt{2})(p_{x1} + p_{x2})$
$\pi_x' = (1/\sqrt{2})(p_{x5} + p_{x6})$	$\pi_x' = (1/\sqrt{2})(p_{x5} + p_{x6})$
$\pi_z = (1/\sqrt{2})(p_{z1} + p_{z2})$	$\pi_z = (1/\sqrt{2})(p_{z1} + p_{z2})$
$\pi_z' = (1/\sqrt{2})(p_{z4} + p_{z5})$	$\pi_z' = (1/\sqrt{2})(p_{z5} + p_{z6})$

In the above formulas, $p_{\xi i}$ is the p_ξ atomic orbital at the carbon center C_i.

For symmetry reasons, the analysis of the PE spectrum of **5** is easier to perform, and the following symmetry adapted π-orbitals are expected within C_{2h} symmetry:

$$\Psi_1 = (1/\sqrt{2})(\pi_x + \pi_x') \quad B_u$$
$$\Psi_2 = (1/\sqrt{2})(\pi_x - \pi_x') \quad A_g$$
$$\Psi_3 = (1/\sqrt{2})(\pi_z + \pi_z') \quad A_u$$
$$\Psi_4 = (1/\sqrt{2})(\pi_z - \pi_z') \quad B_g$$

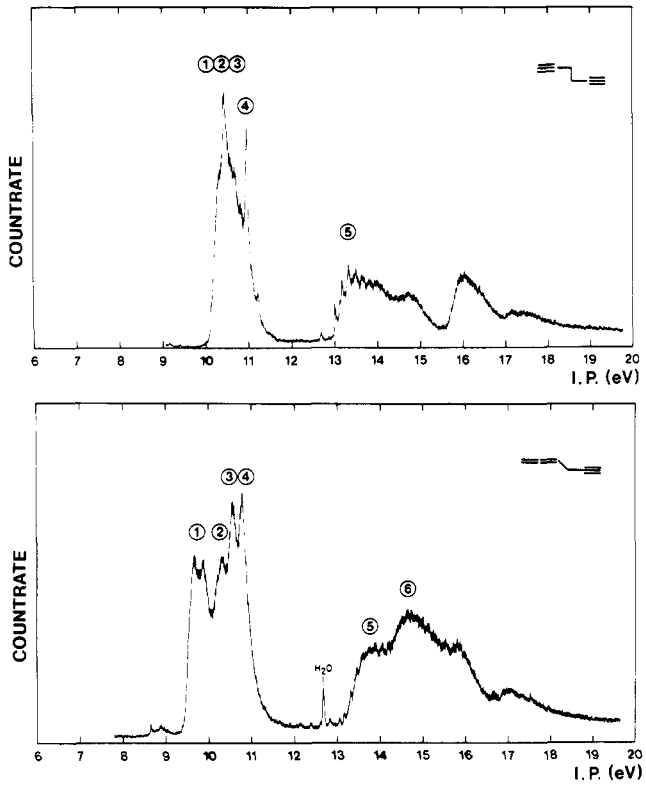


Figure 6. PE spectra of 1,2-hexadiene-5-yne (propargylallene, **4**) and 1,5-hexadiyne (bipropargyl, **5**).

Table V. Comparison between Measured Vertical Ionization Potentials, $I_{v,J}$, and Calculated Orbital Energies for 4 and 5 Using the EH Method (all values in eV)

Compound	Band	Orbital	$I_{v,J}$	$-\epsilon_J$[EH]
$4(C_s)$	1	$a''(\Psi_3,\pi)$	9.65	12.59
	2	$a'(\Psi_2,\pi)$	10.30	12.73
	3	$a'(\Psi_1,\pi)$	10.55	13.23
	4	$a''(\Psi_4,\pi)$	10.79	13.31
	5	$a'(\sigma)$	13.80	13.95
$5(C_{2h})$	1	$a_g(\Psi_2,\pi)$	10.48	12.85
	2	$a_u(\Psi_3,\pi)$		13.24
	3	$b_g(\Psi_4,\pi)$		13.24
	4	$b_u(\Psi_1,\pi)$	10.98	13.37
	5	$a_g(\sigma)$	13.34	13.96

Ψ_3 and Ψ_4 are expected to mix by comparable amounts with the C–H σ-orbitals thus yielding two nearly degenerate orbitals. Ψ_2 again will suffer σ–π mixing with the central carbon–carbon σ-orbital (e.g., "through bond" coupling), *while only* Ψ_1 *cannot have any close lying* σ*-orbital and will therefore be lower in energy than the remaining three* π*-orbitals!*

This expectation of three close lying ionization potentials followed by a unique one is indeed strikingly illustrated by the measured PE spectrum. It is furthermore supported by the fact that the band shape of band 4 suggests that it is due to an ejection of an electron out of a "typical" (e.g., σ–π orthogonal) acetylenic π-orbital. From this spectrum we conclude, that the basis orbital energies of the acetylenic π-orbitals are about

$$\epsilon(\pi_x) = \epsilon(\pi_z) \simeq -10.98 \text{ eV}$$

This is about 0.4 eV higher than the π-orbital energy of acetylene[26] due to electronic back-donation from the linking methylene groups.

σ–π-Conjugation ("hyperconjugation") is responsible for an additional shift of 0.5 eV to give the measured IP of 10.48 eV. This value is comparable to the π-ionization potential of methylacetylene reported to be 10.37 eV.[27] The somewhat lower value found for **5** can be explained by increased unsaturation[28] of **5** as compared to methylacetylene.

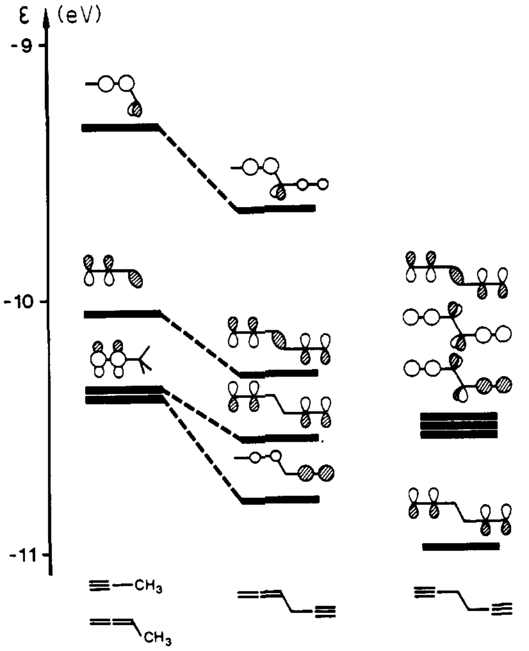


Figure 7. Comparison between the first bands of the PE spectra of methylallene and methylacetylene (left) with those of **4** (middle) and **5** (right).

We wish to conclude our discussion with the assignment of the PE spectrum of propargylallene (**4**). In this molecule, π_x and π_x' are through bond coupled in about the same manner as in biallenyl (**1**), while in contrast to **1**, π_z and π_z' are homoconjugated double bonds. Because of lack of symmetry, the symmetry adapted MO's cannot be chosen in such a simple form as for the previous molecules. In a more general form they can be written as:

$$\Psi_1 = N_1(\pi_x + \lambda_1\pi_x')$$
$$\Psi_2 = N_2(\pi_x - \lambda_2\pi_x')$$
$$\Psi_3 = N_3(\pi_z + \lambda_3\pi_z')$$
$$\Psi_4 = N_4(\pi_z - \lambda_4\pi_z')$$

where λ_i is the mixing coefficient and N_i the normalizing constant of Ψ_i. In a first approximation we can derive the MO's of **4** from those of a perturbed methylallene[9] and methylacetylene.[27] Substitution of a H atom by an acetylenic moiety or an allenic moiety respectively will raise the ionization potentials of both fragments. This is indicated on the left of Figure 7. This qualitative consideration yields that the HOMO of **4** must be the "inner" allenic π-orbital. This is in accordance with EH (see Table IV and Figure 7), MINDO/3, and CNDO/2 calculations.

Furthermore, this assignment is corroborated by the vibrational fine-splitting of band 1 in the PE spectrum. The vibrational spacing $\Delta\nu(M^+) = 0.2$ eV is in line with the one observed in biallenyl ($\Delta\nu(M^+) = 0.22$ eV), where the assignment of the bands is quite unambiguous. This suggests that **4** should react toward electrophilic attack as an allene derivative rather than an acetylene derivative.

Experimental Section

The preparation of **1**,[4] **3**,[22] **4**,[4] and **5**[4] has been described in the literature. Compound **2** has been prepared by Cu^{I}Cl-catalyzed addition of allenyl magnesium bromide to 1-bromo-2-butyne.[29]

The PE spectra were recorded on a PS 18 photoelectron spectrometer (Perkin-Elmer Ltd., Beaconsfield, England) of the type described by Turner.[30]

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie, Deutsche Forschungsgemeinschaft, and by the Otto Röhm Stiftung.

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^1H and ^{13}C Nuclear Magnetic Resonance Spectra of Heteroaromatic Carbocations. Xanthylium Ions

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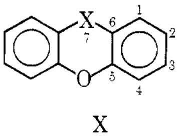
Received December 16, 1974

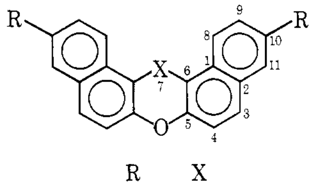
Abstract: The ^{13}C NMR spectra of highly stable xanthylium derivatives were measured and completely assigned with the use of double resonance technique and chemical shift criteria. The observed shifts, correlated with the total charge density calculated from CNDO, show an extensive delocalization of the positive charge.

The aryl carbonium ions are the best investigated carbonium ions. Their structures have been determined by a variety of spectroscopic methods.[2] In contrast, few data are available for heteroaromatic carbonium ions; particularly the xanthylium derivatives are much less known and have not yet been directly characterized. The only exception is that of xanthylium ion for which Deno and his coworkers reported[3] the uv absorption spectrum in concentrated sulfuric acid.

In view of the current interest in the synthesis[4] and reactivity[5,6] of some xanthen-9-yl derivatives, we have undertaken a spectroscopic study, based on NMR, which is customarily considered one of the best sources of information in studying the structure and the charge distribution of carbocations.[7]



	X
1,	CH^+
4,	CH_2



	R	X
2,	H	CH^+
3,	Br	CH^+
5,	H	CH_2
6,	Br	CH_2

We report here a detailed analysis of the proton and carbon NMR spectra of the already known xanthylium ion **1** and of the highly stable ions **2** and **3**. The latter two compounds are involved as intermediates in a new recently described regiospecific reaction of substituted phenol salts[8] and are sufficiently stable to be isolated as deep red crystals.

While providing additional experimental evidence of their ionic structures, we suggest an interpretation of the observed chemical shifts in terms of positive charge density and ring current effect.