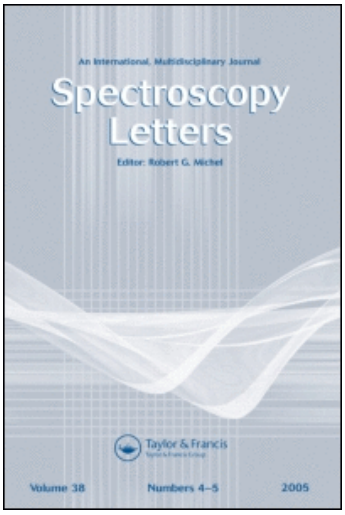

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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Peter C. Burgers[a]; Cor W. Worrell[a]; Marinus P. Groenewege[a]
[a] Laboratory for General Chemistry, (Molecular Spectroscopy), Utrecht, The Netherlands

To cite this Article Burgers, Peter C. , Worrell, Cor W. and Groenewege, Marinus P.(1980) 'On the Ceometry and Electronic Structure of Methyl Allenyl Ether and Methyl Allenyl Thioether', Spectroscopy Letters, 13: 6, 381 — 396
To link to this Article: DOI: 10.1080/00387018008064030
URL: http://dx.doi.org/10.1080/00387018008064030

SPECTROSCOPY LETTERS, 13(6), 381-396 (1980)

ON THE GEOMETRY AND ELECTRONIC STRUCTURE OF METHYL ALLENYL ETHER AND METHYL ALLENYL THIOETHER

by

Peter C. Burgers, Cor W. Worrell and Marinus P. Groenewege
Laboratory for General Chemistry, (Molecular Spectroscopy)
Transitorium 3, Padualaan 8, 3508 TC Utrecht, The Netherlands.

ABSTRACT

The He(I) photoelectronspectra of methyl allenyl ether and its sulphur analogue furnish information on lone pair (n)/π conjugation. Evidence is presented that methyl allenyl ether in the gas-fase exists in two conformations being for a major part the stable s-cis and to a minor degree the s-trans rotamer. Empirical calculations (MIEHM) substantiate our proposals, whilst a semi-empirical method (MINDO/3) is not in disagreement with it. Our result is in contradiction with previous electron diffraction work.

INTRODUCTION

A few years ago Derissen en Bijen[1,2] published electron diffraction work on unsaturated ethers en thioethers from which they were able to deduce the molecular geometries of these compounds. As is well known detailed knowledge of molecular geometries is a

first requirement for the interpretation and calculation of NMR- and infrared spectra which in their turn are indispensible for the elucidation of reaction mechanics occuring in solution chemistry[1].

Reactions in solution chemistry in most cases involve charged intermediates. Our knowledge of the most conformations of these charged intermediates is however obscured by the intermolecular collision they undergo before the final state of the product is reached. A better knowledge of the structure of isolated organic ions is therefore of fundamental value to reaction chemistry. The electronic structure of molecules in the gas phase and very often also the geometry can be elucidated by the combined approach of photoelectron spectroscopy and molecular orbital calculations[3].

This paper presents an investigation of the electronic structure and geometry of methyl allenyl ether, its sulphur analogue and a higher homologue, they constitute a class of compounds not investigated previously. Discussions are given for the individual compounds.

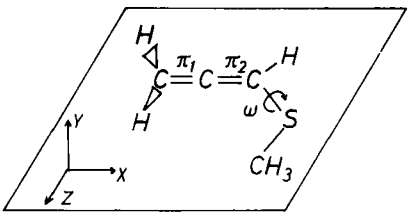
RESULTS AND DISCUSSION

The following compounds were investigated:

$CH_2=C=CH-X-R$	X	R	
	S	CH_3	(1)
	O	CH_3	(2)
	O	$t\text{-}C_4H_9$	(3)

Methyl allenyl thioether (1)

The molecular orbitals of (1) are defined in Fig. 1 and the He (I) photoelectron spectrum together with the accurate ionization energies and assignments is given in Fig. 2.



π_1 : *in (x,z) plane*

π_2 : *perpendicular to (x,z) plane*

$n_\perp$: *sulphur lone pair perpendicular to (C-S-C) plane*

n_o : *sulphur lone pair in (C-S-C)plane*

ω : *torsion angle*

Fig.1. Definition of the molecule orbitals of (1) and the torsion angle ω.

As can be seen from fig. 2 four bands with an intensity ratio of 1.2 : 1 : 1 : 1 can easily be distinguished. The second band possesses a well resolved vibrational structure with spacings of 1300 cm^{-1}; this frequency is reduced by 33% in comparison to that of the neutral molecule (1950 cm^{-1}) and is assigned to the ionic asymmetrical -C=C- stretching vibration. This rather large reduction can be rationalized by a lowering of the force constant in one of the -C=C- oscillators as a result of the ionization process and consequently by a reduction of the coupling between the two -C=C- oscillators.

The first band shows a vibrational progression of 600 cm^{-1} due to the -C=C=C- ionic bending vibration indicating a reduction of 30% in comparison to the molecular bending vibration. The presence of a -C=C- stretching mode which is expected to possess

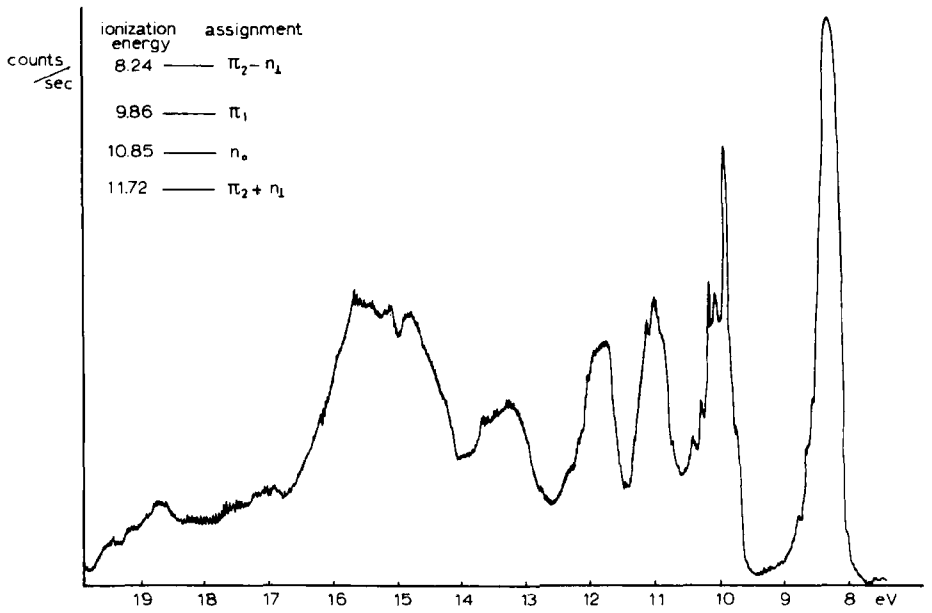


Fig. 2. He (I) photoelectron spectrum of methyl allenyl thioether

an ionic frequency of approximately 1200 cm^{-1} can however not be ruled out.

From simple molecular orbital considerations (Fig. 3) involving interaction of the sulphur $n_{\perp}$ and the π_2 system the orbital requiring the least energy for ionization is expected to be the $\pi_2 - n_{\perp}$, followed by π_1 and finally the one containing the sulphur in plane lone pair n_σ and $\pi_2 + n_{\perp}$.

Taking the molecule planar (s-cis or s-trans) this ordering is indeed substantiated by MIEHM and MINDO/3 calculations (vide infra). As expected solely on the basis of energy difference of the sulphur non-bonding n and allenic π_2 orbitals (energies -8.8

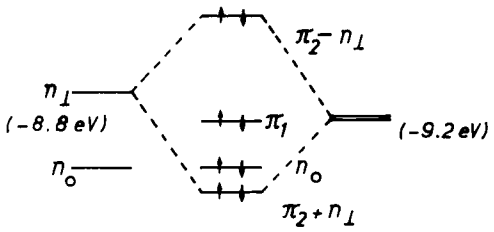


Fig. 3. Molecular orbital digram of methyl allenyl thioether.

and -9.2 eV respectively), the highest lying ionization energy is predicted to be mainly due to the $n_\perp$ orbital, while for the lowest lying ionization a major contribution from the π_2 electrons is calculated.

From an earlier gas electron diffraction study[1] on the molecular structure of (1) it was concluded that a model with only one planar syn conformation was insufficient to explain the experimental intensity curves. It was necessary to introduce a second non-planar conformation which was expected to have a torsion angle ranging from 45 to 75° and to be present for about 30 mol%. Earlier CNDO/2 calculations on methyl vinyl thioether[5] revealed a strong dependence of the $\pi_{C=C}$ orbital energy upon the torsion angle, increasing strongly from 0° (C_s symmetry) to 90° (C_1 symmetry). On the basis of these results we thought it worthwhile to perform calculations on on (1) at various torsion angles. The result is shown in Fig. 4a en Fig. 4b.

As can be seen from Fig. 4a the orbital energy corresponding to $\varepsilon_4(\pi_2 + n_\perp)$ is indeed quite sensitive to the torsion angle ω.

In Fig. 4c the MIEHM calculated separations of ε_2 and $\varepsilon_3(\Delta\varepsilon_{23})$

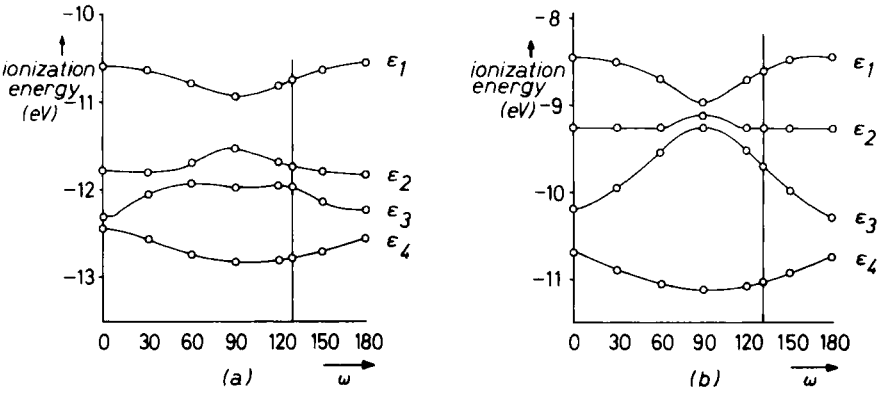


Fig. 4 a-b

Ionization energies of methyl allenyl thioether as function of the torsion angle ω, calculated by MIEHM (a) and MINDO/3 (b).

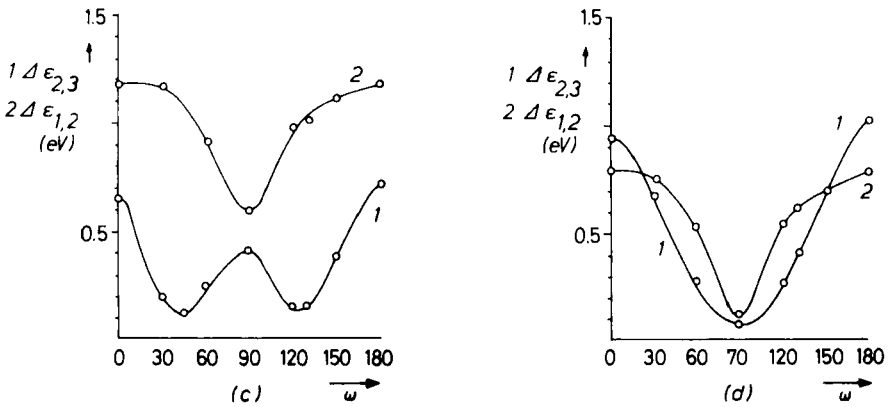


Fig. 4 c-d

Seperations of ε_1 and ε_2 (item (I)) and of ε_2 and ε_3 (item (2)) as a function of ω, calculated by IEHM (c) and MINDO/3 (d).

at various torsion angles are shown (item (1)). It can readily be seen that at all torsion angles corresponding to a non-planar configuration the calculated splitting is found to be substantially less than the experimental value (0.99 eV) while those corresponding to the planar cis and trans configurations are closest (0.66 and 0.74 resp.). Conformations possessing rotational angles between 45 and 75° are predicted to have, at best, moderate (0.4 eV) splitting of ε_2 and ε_3 which does not fit in with the experimental result.

The calculated separations of ε_1 and ε_2 at various torsion angles are shown as item (2) in Fig. 4c. Although a serious discrepancy between calculated and experimental value is found at all angles, it is smallest (0.4 eV) for a planar conformation and largest for severe non-planarity (1.0 eV at $\omega = 90^{\circ}$).

MINDO/3 calculations predict the orbital energy of the sulphur lone pair electron (ε_3) to be the most sensitive to variation of the torsion angle (Fig. 4b). At large deformations from planarity the second (π_1) and third band are calculated at similar energies. For a planar conformation the calculated separations between ε_2 and ε_3 are largest (0.95 eV for s-cis and 1.04 eV for s-trans, experimental value 0.99 eV, see Fig. 4d, item (1)). This also holds for the calculated seperations of ε_1 and ε_2 (Fig. 4d, item (2)).

As a consequence, photoelectron spectral measurements combined with semi-empirical (MIEHM, MINDO/3) calculations do not

indicate the presence, to an appreciable extent, of a conformation severly deformed from planarity.

From the MIEHM calculated eigenvectors it appears that interaction of the π_1 and $\pi_2 + n_{\perp}$ electrons in the region $\omega = 125^{o}$ to $\omega = 135^{o}$ is so pronounced that it is hardly significant to differentiate between a π_1 and a $\pi_2 + n_{\perp}$ system. Interaction between these orbitals is indeed forbidden in a conformation possessing C_s symmetry ($\omega = 0^{o}$ and $\omega = 180^{o}$) but as soon the symmetry is lowered interaction may occur. In fact, at lower symmetry all orbitals corresponding to ε_1, ε_2, ε_3 and ε_4 more or less interact.

Methyl allenyl ether (2)

The overall appearance of the photoelectron spectrum of (2) (Fig. 5) differs from that of (1) in so far as the third and fourth bands are concerned. As can be seen they almost coincide, thus giving rise to one band with twice the area of the first band.

As was found for compound (1) the vibrational structure of the second band is well resolved: a wavenumber of 1250 cm^{-1} is observed and is assigned to the ionic asymmetrical -C=C- (π_1) stretching vibration. This would indicate a reduction in frequency of about 36% (again a rather high value) from the molecular vibration which was found at 1960 cm^{-1}. MINDO/3 calculations give the ordering $\pi_2 - n_{\perp}$ (ε_1), π_1 (ε_2), n_{σ} (ε_3) and $\pi_2 + n_{\perp}$ (ε_4), see Fig. 6b, while MIEHM calculations predict predominant $n_{\perp}$ character for the first band, assign the second band to n_{σ}, the third

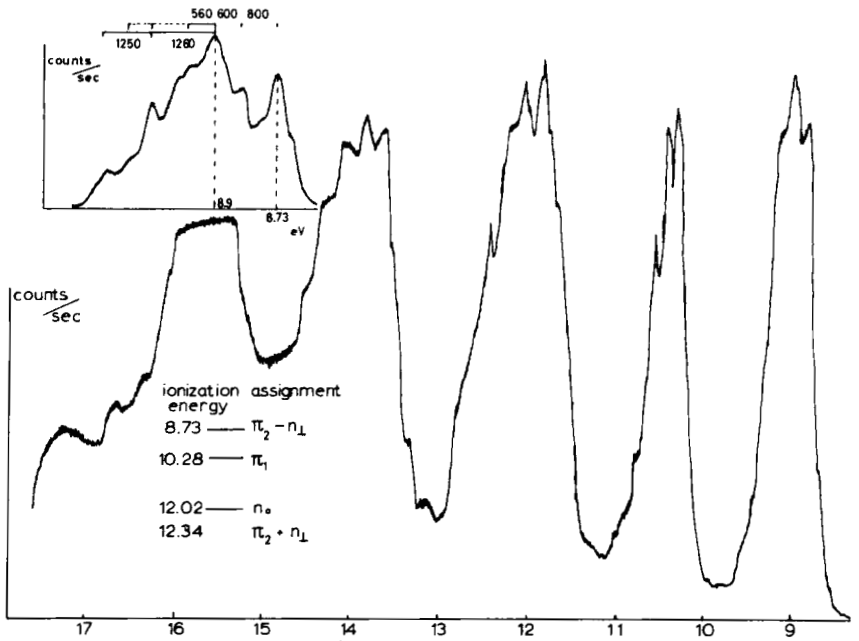


Fig. 5. He (I) photoelectron spectrum of methyl allenyl elther inset first band on extended scale.

to π_1 and the fourth to π_2 (Fig. 6a). In view of earlier observations we argue that the second and the third assignment of the MIEHM results should be interchanged.

At first glance the vibrational structure as well as the intensity ratio's of the vibrational components of the first band seems rather complex (see inset Fig. 5).

A high probability for the 0 - 0 transition upon ionization can be outruled since the complex nature disappears when dealing with compound (3) (Fig. 7), in which R is a bulky t-C_4H_9 group.

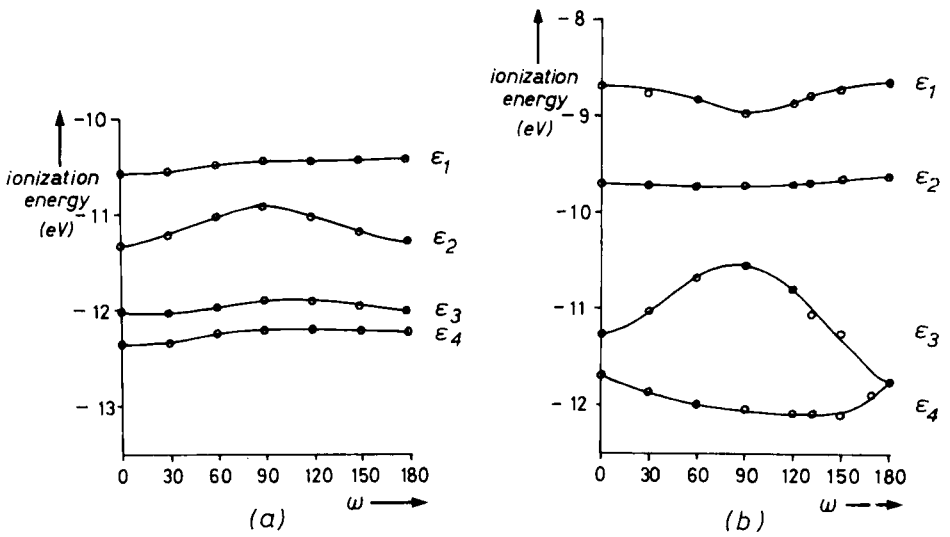


Fig. 6. Ionization energies of methyl allenyl ether as a function of torsion angle ω, as calculated by MIEHM (a) and MINDO/3 (b).

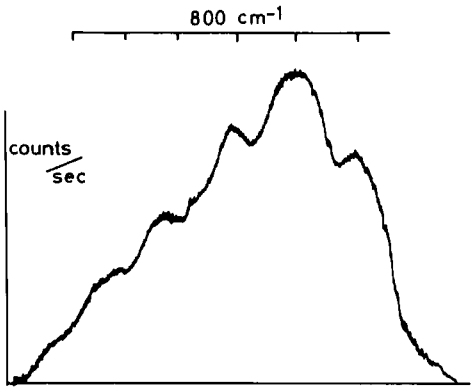


Fig. 7. First band of the Photoelectron spectrum of t-butyl allenyl ether

For bulky R groups steric hindrance makes a s-trans conformation or a conformation severely deformed from the s-cis the only plausible one. Although it seems in contradiction with earlier gas electron diffraction work[2] from which it was concluded that only one model with a s-cis conformation was sufficient to explain the experimental intensity curves, the question rises whether we are dealing with two conformations a and b each contributing at a given temperature in a fixed amount to the photoelectron spectrum; a would require a first ionizing energy of 8.73 eV and b of 8.90 eV (inset Fig. 5). For a a vibrational wavenumber on the first band of 800 cm^{-1} is observed (tentatively assigned to a C=C=C- ionic bending mode), whereas possibly two progressions are found for b, namely 1200 cm^{-1} (-C=C- asymmetric stretch) and 560 cm^{-1} (-C=C=C- bending).

Further arguments in favour of our proposal and for the structure of a and b come from the following observations:

1. From our experiments the absolute difference in the first ionization energies for a and b would be 0.17 eV, probably to small to be substantiated by semi-empirical calculations, although both MINDO/3 and MIEHM predict the s-trans conformation to have the higher first ionization energy (MINDO/3 s-cis: -8.72 eV, s-trans: -8.67 eV; MIEHM: s-cis: -10.59 eV, s-trans: -10.44 eV). More noteworthy is the MIEHM calculated separation of ε_1 and ε_3, which for the s-cis conformation amounts to 1.43 eV and for s-trans to 1.55 eV (Fig. 8). These calculated figures are only compatible

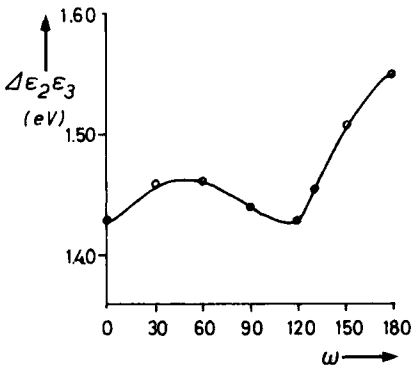


Fig. 8. Splittings of ε_1 and ε_3 for methyl allenyl ether as function of torsion angle ω.

with the experimental ones (1.40 and 1.55 eV) if the higher ionization energy belongs to the s-trans conformation i.e. to a. Moreover, the corresponding separation in compound (3), which can not attain the s-cis conformation amounts to 1.51 eV (calculated, s-cis: 1.43; s-trans: 1.52 eV).

2. The experimental v.s. MIEHM calculated energies of the π_1 and $\pi_2 - n$ for (2) can only yield a linear relationship if the higher ionization energy corresponds to the s-trans conformation (Fig. 9).

3. Infra red data obtained for methyl vinyl ether in the gas- and liquid fase[6,7] as well as theoretical calculations[8,9] for this compound led to the conclusion that the molecules of this ether exist to a large (if not exclusive) extent in the s-cis conforma-

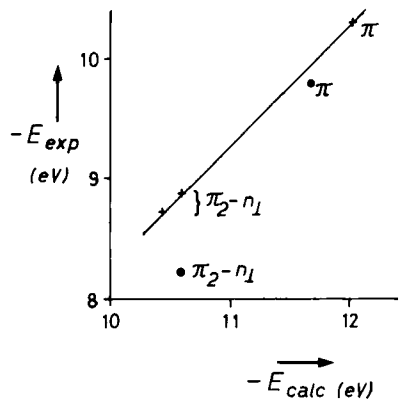


Fig. 9. Experimental versus calculated ionization energies of the $\pi_2 - n_-$ and π_1 orbitals.
+ : methyl allenyl ether, o : methyl allenyl thioether.

tion. We tentatively argue that this also holds for the allenyl ether and considering the intensity ratio's of the two components of the first band in the photoelectron spectrum of (2) (inset Fig. 5) it is then concluded that the higher ionization energy belongs to the s-trans rotamer.

In some instances infra red experiments can yield valuable information on molecular geometries and this was applied with considerable succes to α,β-unsaturated ethers[6,7,10,11]. The infra red spectra of (2) taken in the gasphase at temperature ranging from 20° to 150°C do not indicate the excistence of the two conformations.

Recent NMR-studies in the liquid phase [12] indicated that at room temperature compound (1) exists largely or even exclusively in the s-cis conformation, but no precise data were given.

Additionally the t-C_4H_9 ether was found to exist in one conformation, most probably and most surprisingly the s-cis conformation, although this was not stated explicitly.

A final mark concerns the relative stability of ions a and b in the ground state. For the vinyl ether it was found that for the neutral molecules the s-cis conformation is more stable[6] by (1.1 ± 0.3) kcal mol^{-1}. If the corresponding value for the allenyl ether does not exceed 3.9 kcal mol^{-1} (0.17 eV) then ions in the ground state having the s-trans conformation are expected to have the lower heat of formation.

CONCLUSION

Although it is true that electron diffraction work, IR studies and NMR measurements can considerably aid the elucidation of molecular geometries, photoelectron spectroscopy should not be underestimated in this respect. Electron diffraction and IR results do not indicate the presence of a second rotamer of methyl allenyl ether but our analyses of the photoelectron spectrum of methyl allenyl ether and of the calculated changes in the position of the electronic levels accompanying conformational changes do provide evidence for the existence to an appreciable extent of a second rotamer. It is also concluded that this second rotamer has the s-trans conformation or that it is not deformed very much from this planar configuration.

EXPERIMENTAL

The photoelectron spectra were recorded on a Vacuum Generator ESCA-2 spectrometer at a resolution of 0.02 eV using He (I) emission as ionizing source. Calibration was done by Xe as internal standard. The compounds were synthesized via standard procedures[13]. The purity was checked by NMR and mass spectroscopy.

Calculations of the orbital energies were carried out following the MIEHM[14] and MINDO/3[15] method. Molecular coordinates were taken from ref. 1 and 2.

ACKNOWLEDGEMENTS

We thank Miss J. Bouwstra and Mrs. L. de Korte for performing some of the calculations, Dr. D. Zijp for valuable discussion and Dr. H. Hommes for his kind gift of some of the samples.

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Received: March 18, 1980
Accepted: April 15, 1980