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1. Santesson, R. *Symbolae Botan. Upsalienses* **12** (1952) 1.
2. Santesson, J. *Acta Univ. Ups., Abstr. Upps. Diss. Sci.* **127** (1969) 1.
3. Santesson, J. *Arkiv Kemi* **30** (1969) 363.
4. Santesson, J. *Acta Chem. Scand.* **21** (1967) 1162.
5. Bohman, G. *Phytochemistry* **8** (1969) 1829.
6. Santesson, J. *To be published.*
7. Bendz, G., Bohman, G. and Santesson, J. *Acta Chem. Scand.* **21** (1967) 2889.
8. Yosioka, I., Yamauchi, H., Morimoto, K. and Kitagawa, I. *Tetrahedron Letters* **1968** 1149.
9. Bruun, T., Hollis, D. P. and Ryhage, R. *Acta Chem. Scand.* **19** (1965) 839.
10. Culberson, C. *Chemical and Botanical Guide to Lichen Products*, Univ. of N. Carolina Press, Chapel Hill 1969.
11. Santesson, J. *Arkiv Kemi* **31** (1969) 57.
12. Huneck, S. and Santesson, J. *Z. Naturforsch.* **24b** (1969) 756.
13. Santesson, J. *Phytochemistry* **9** (1970). *In press.*

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The Single and Double Bonds between sp^2 -Hybridized Carbon Atoms, as Studied by the Gas Electron Diffraction Method

VI. The Molecular Structure of Acrolein

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The molecular structure of acrolein is a natural choice for inclusion in the present research series. The molecular structure of this molecule was studied by microwave spectroscopy in 1966¹ and more recently by electron diffraction.² When the latter results appeared, however, the experimental part of the investigation reported here was already carried out, and it was decided to continue the structure study. Even if the structural results may be of somewhat reduced interest, it might be worth while to compare results obtained by different electron diffraction laboratories.

The experimental data for the electron diffraction study of acrolein were recorded at two camera distances, approximately 48 cm and 19 cm. The data were combined to give an experimental molecular intensity function ($sM(s)$ -function) in the s -range 1.25–45.0 Å⁻¹. The molecular structure was studied by least squares refinements of the experimental molecular intensity function and by following the progress on radial distribution functions. In the structure analysis all C=C–H angles were assumed to be equal and the CH bond distance in the aldehyde group was assumed to be 0.02 Å larger than the other CH bond distances.

Table 1 lists the final results for the internuclear distances and mean amplitudes of vibrations for acrolein. The distances are arranged in order of increasing internuclear distance so that it will be easy to identify them in Figs. 3 and 4 which show the experimental and theoretical radial distribution functions when two different damping constants are applied. The solid bars represent relative contributions from the internuclear distances listed in Table 1.

Table 1. Observed internuclear distances and mean amplitudes of vibrations for acrolein. (All values are given in Å units).

Distance	$r_g(1)$	$\sigma(r_g(1))$	u	$\sigma(u)$
C ₂ -H ₂	1.0787	0.0021	0.0776	0.0020
C ₁ -H ₁	1.0987		0.0790 ^a	
C=O	1.2093	0.0006	0.0382	0.0006
C=C	1.3401	0.0011	0.0439	0.0008
C-C	1.4807	0.0013	0.0548	0.0010
O...H ₁	1.9964		0.1000 ^a	
C ₂ ...H ₃	2.1153		0.1000 ^a	
C ₂ ...H ₁	2.1924		0.1000 ^a	
C ₁ ...H ₂	2.2098		0.1000 ^a	
O...C ₂	2.3860		0.0636 ^a	0.0015
C ₁ ...C ₃	2.4420		0.0787	0.0027
C ₃ ...H ₁	2.6368		0.1400 ^a	
C ₁ ...H ₃	2.6674		0.1600 ^a	
O...H ₂	2.6917		0.1375 ^a	
C ₁ ...H ₃ ¹	3.4402		0.1000 ^a	
O...C ₃	3.5566		0.0722	0.0024
O...H ₃	3.8651		0.1300 ^a	
O...H ₃ ¹	4.4798		0.1200 ^a	

^a Assumed values.

The numbering of the atoms in acrolein is illustrated in Fig. 1. Table 1 and Figs. 3 and 4 include all internuclear distances except the hydrogen-hydrogen distances. Some of the mean amplitudes of vibrations in Table 1 are marked with an index *a*. They are assumed values and are approximately the same as *u*-values calculated from spectroscopic data.³

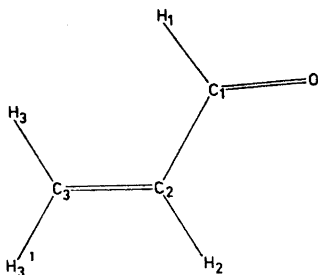


Fig. 1. Acrolein. Molecular model which shows the numbering of the atoms.

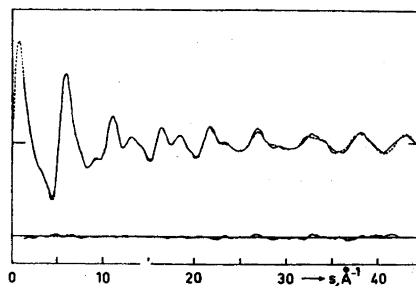


Fig. 2. Acrolein. Experimental (—) and theoretical (---) molecular intensity functions and the difference between them.

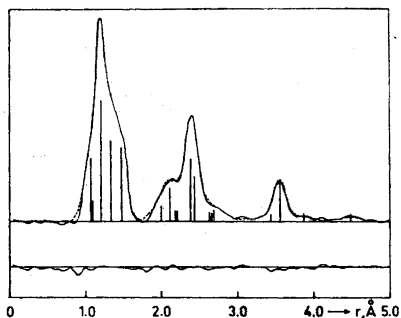


Fig. 3. Acrolein. Experimental (—) and theoretical (---) radial distribution functions and the difference between them. Artificial damping constant: 0.0009.

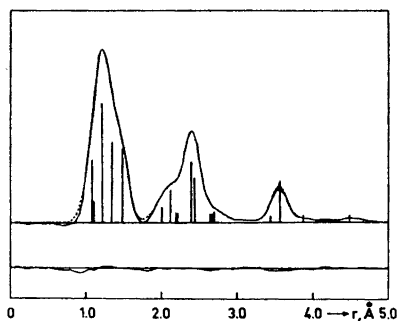


Fig. 4. Acrolein. Experimental (—) and theoretical (---) radial distribution functions and the difference between them. Artificial damping constant: 0.0024.

Table 2. Comparison of structural results for acrolein. (Bond lengths in Å units and angles in degrees).

Parameter	Present study	St.dev. ^a	Ref. 1 (MW) ^b	Ref. 2 (ED) ^c
C ₁ -H ₁	1.0987 ^d		1.108±0.003	1.123±0.027
C ₂ -H ₂	1.0787	0.0021	1.086±0.005	1.094±0.010
C=C	1.3401	0.0011	1.345±0.003	1.335±0.005
C-C	1.4807	0.0013	1.470±0.003	1.478±0.005
C=O	1.2093	0.0006	1.219±0.005	1.208±0.003
∠CCC	119.85	0.371	119.83±0.167	121.0±0.7
∠CCO	124.69	0.230	123.27±0.333	124.0±0.7
∠C=C-H	121.59	1.711	121.42±0.167 ^e	120.7±1.3
∠C ₂ C ₁ H ₁	115.62	1.002	115.10±0.167	114.7±1.3

^a The standard deviations are results from the least squares refinements of all parameters simultaneously. ^b r_s Structure. ^c Zero-point average structure. ^d C₁-H₁ assumed to be 0.02 Å larger than C₂-H₂. ^e Average of the three C=C-H angles.

The experimental molecular intensity function is shown in Fig. 2 together with the theoretical $sM(s)$ -function calculated for the final molecular model.

Cherniak and Costain¹ report a negative value for the ground state inertial defect ($\Delta = -0.0212 \text{ amu} \cdot \text{Å}^2$) in their microwave study of acrolein. They state that this might be an indication that the molecule is not exactly planar, but conclude that other observations make it reasonable to assume that acrolein has a planar *trans* structure. When non-planarity is allowed for in the present least squares refinements, a torsion angle of 11.2° around the C₁-C₂ bond gives slightly better results than an all-planar molecular model. The torsion angle around C₁-C₂ leads to reductions in the longer internuclear distances which are of the same order of magnitude as might be expected because of shrinkage effects.⁴ (The O...C₃ distance is for example reduced from 3.5628 Å to 3.5566 Å.) As a result of the present study it can therefore be concluded that the molecule does not deviate significantly from a planar *trans* conformation.

In Table 2 the molecular parameters obtained in the present investigation are compared with the recently reported microwave¹ and electron diffraction² results. The standard deviation values listed in column 3 are those resulting from the least square refinements when all param-

eters were varied simultaneously and when a diagonal weight matrix was applied. The error limits for the determined parameters are probably about three times larger than the standard deviation values. It will be seen from Table 2 that the observed bond distances are in best agreement with the results of Kuchitsu *et al.*² while the observed bond angles correspond most closely to those determined by Cherniak and Costain.¹ All the observed parameters are, however, in satisfactory agreement with both the earlier structure studies.

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1. Cherniak, E. A. and Costain, C. C. *J. Chem. Phys.* **45** (1966) 104.
2. Kuchitsu, K., Fukuyama, T. and Morino, Y. *J. Mol. Structure* **1** (1967-68) 463.
3. Cyvin, S. J., Hagen, G. and Trätteberg, M. *To be published.*
4. Morino, Y., Nakamura, J. and Moore, P. W. *J. Chem. Phys.* **36** (1962) 1050.

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