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A STUDY OF THE MOLECULAR STRUCTURE OF METHYL ALLENYL ETHER BY MEANS OF GAS ELECTRON DIFFRACTION

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ABSTRACT

From the electron diffraction pattern of gaseous methyl allenyl ether at room temperature the following bond lengths and bond angles for the molecular structure were obtained (standard deviations in parentheses): C–C = 1.318 (0.004) Å, C–O = 1.375 (0.007) Å, C′–O = 1.427 (0.008) Å, C–C–O = 125.3 (1.2)°, C–O–C′ = 115.0 (1.2)°.

The best model obtained by a least-squares fit on the molecular intensity curves is a planar *cis*-conformation (C_s symmetry) with a large torsional motion of the OCH_3 group around the other ether linkage, the average of the absolute value of the torsion angle is 23 (6)°. There is no evidence of the presence of other conformations at this temperature.

INTRODUCTION

Unsaturated ethers and thio-ethers are being investigated in our chemical department by Hoff *et al.*[1]. A study of the molecular structures of methyl allenyl ether, methyl allenyl thio-ether and methyl vinyl thio-ether was undertaken to provide accurate molecular geometries of these compounds to serve as background information in the interpretation of reaction mechanisms, infrared and NMR spectroscopical data etc. for this class of compounds.

As these compounds are rather volatile and as their molecular structures are not expected to be too complicated, the method of gas electron diffraction seemed to be the most suited for this purpose. In this paper the results for methyl allenyl ether are given and compared with those for methyl vinyl ether obtained by Owen and Seip[2].

EXPERIMENTAL AND DATA REDUCTION

The sample was obtained from Dr. L. Brandsma *loc. cit.* The electron diffraction patterns were collected at room temperature in the usual way with the Balzers Eldigraph KDG 2 electron diffraction unit[3], kindly placed at our disposal by F.O.M.R.E. and stationed at the State University of Leiden, The Netherlands. The electron wavelength was determined using CO_2 as a reference sample[4]. Diffraction patterns for 40 kV electrons were recorded on Kodak Electron Image plates at camera heights of 50, 25 and 11 cm, and these were photometered on a Joyce–Loebl microdensitometer. The optical densities obtained in this way were treated mainly as described in ref. 5. In this particular case an empirical background function was applied, which was iteratively improved during the subsequent

TABLE 1

EXPERIMENTAL MODIFIED MOLECULAR INTENSITIES FOR METHYL ALLENYL ETHER

A are the data for the 50 cm camera height, ranging from s = 1.75 with steps of 0.25 Å^{-1} to 15.0 Å^{-1}; B for the 25 cm distance (5.00 step 0.25 until 27.00 Å^{-1}) and C for the 11 cm distance (9.75 step 0.25 until 35.75 Å^{-1}).

A.									
+1006	+847	+175	−416	−1014	−1514	−1694	−1750	−1781	−1978
−2135	−1979	−1374	−367	+1022	+2128	+2749	+2833	+2312	+1605
+869	+267	−229	−724	−1178	−1629	−1838	−1657	−1268	−728
−142	+298	+573	+964	+1368	+1566	+1391	+1020	+544	+34
−388	−676	−944	−1122	−1270	−1239	−881	−440	+139	+742
+1124	+1152	+1044	+846						
B.									
−12	+748	+1337	+1789	+1823	+1473	+923	+391	+6	−220
−433	−712	−1029	−1186	−1119	−820	−451	−48	+243	+401
+636	+851	+969	+925	+732	+399	+59	−175	−328	465
−655	−691	−708	−572	−292	+64	+365	+462	+509	+397
+349	+372	+318	+205	+224	+95	−179	−488	−588	−741
−753	−621	−479	−256	+109	+445	+794	+1036	+976	+807
+584	+324	+32	−154	−265	−389	−320	−371	−444	−354
−427	−346	−326	−308	−141	+167	+404	+507	+675	+654
+488	+194	−21	−103	−174	−134	−232	−165	−181	
C.									
+351	+420	+495	+524	+462	+330	+164	−18	−169	−283
−377	−476	−536	−481	−287	−98	+87	+320	+468	+426
+330	+263	+197	+155	+128	+78	+5	−120	−207	−300
−374	−379	−371	−316	−185	−31	+187	+444	+613	+636
+542	+419	+251	+83	−26	−74	−123	−191	−239	−277
−342	−410	−407	−308	−176	−31	+148	+304	+449	+501
+369	+264	+73	−105	−138	−169	−156	−139	−139	−108
−59	−28	−3	−3	−70	+13	+143	+208	+247	+235
+232	+113	−6	−28	−101	−132	−114	−56	−47	−72
−69	−52	−33	−87	−88	+6	+18	+33	+60	+109
+130	+84	+69	+38	−42					

analysis. The atoms k and l in the modification factor $s/[f(k) \times f(l)]$ were chosen as C and O, and all scattering factors were taken from Cox and Bonham's tables[6].

The modified molecular intensities extended from $s = 1.75$ to $s = 35.75$ Å^{-1} and these are listed in Table 1. The experimental radial distribution function obtained by Fourier inversion of these intensities is shown in Fig. 1.

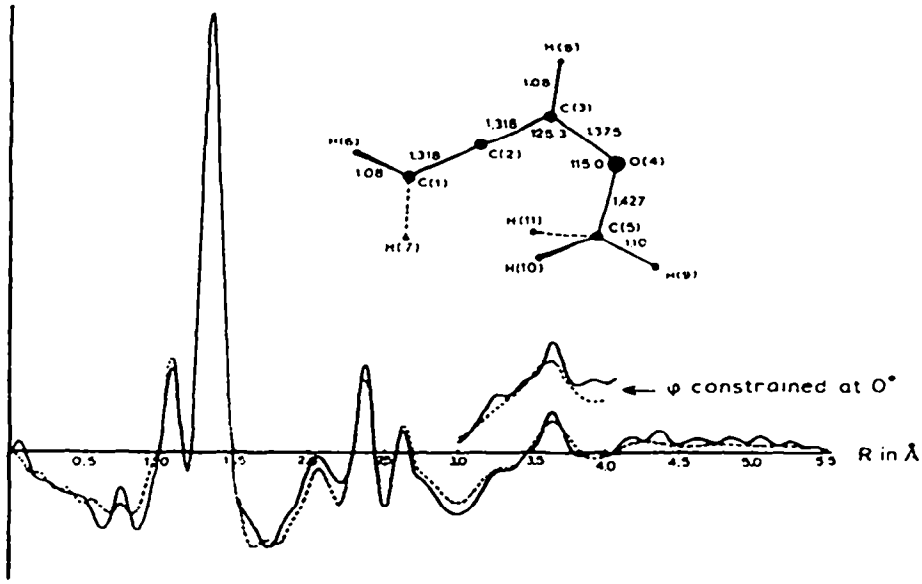

Fig. 1. Undamped radial distribution function for methyl allenyl ether. (———) = experimental (- - -) — calculated.

STRUCTURE ANALYSIS

The values of the structural parameters needed to define a model for the molecular geometry of methyl allenyl ether were derived from the radial distribution function. The peak at 1.1 Å corresponds to the CH bond lengths, the composite peak at 1.37 Å contains all the other bond distances. The peaks at higher r values corresponding to non-bonded distances are also composite. However, all these peaks can be attributed to intramolecular distances between atoms in a planar *cis*-conformation as drawn in Fig. 1. There is no evidence of any other conformation at this temperature.

In the model used to calculate a theoretical radial distribution function, the CH_3 group was assumed to have local C_{3v} symmetry, its axis coinciding with the CO bond. The CH_2 group was assumed to have C_{2v} symmetry and to be at right angles to the C(1)–C(3)–H(8) plane, as it is in allene[7]. H(8) atom was located in such a way that its CH bond bisects the C=C–O angle. All these assumptions concerning the hydrogen atoms are supported by the low scattering power of

hydrogen atoms for electrons, which causes the diffraction pattern to be insensitive to small changes in H-atom locations.

A torsional motion around the C(3)–O(4) bond was described by means of a rotational angle ϕ and in the same way a CH_3 rotational angle α was included; however, the latter angle was constrained at 0° to minimize the H–H contacts, because it was impossible to determine its value.

A possible difference in the two C–C bond lengths could not be detected (we refined such a difference, but the result was 0.01 Å with a standard deviation of 0.02 Å, while all other parameters remained nearly unchanged). Therefore in the refinements these two distances were considered to be of equal length.

To be able to carry out least squares refinements of the parameter values, some additional assumptions concerning the root mean square amplitudes of vibration (u values) had to be made. Most of these values were transferred from analogous molecules. An average value was refined for the remaining amplitudes. For the bond distances C–C, C(3)–O(4), C(5)–O(4) initial values of 0.038, 0.047, 0.051 Å were chosen and the differences between these values were taken as constraints in the refinements.

The parameters resulting from the least squares procedure are presented in Table 2; the standard deviations listed are those obtained from the normal equa-

TABLE 2

MOLECULAR PARAMETERS FOR METHYL ALLENYL ETHER OBTAINED BY THE LEAST SQUARES METHOD

Parameter	*Value*	*Stand. dev.*	*u Parameter*	*Value (Å)*	*Stand. dev. (Å)*
C(1)–C(2)	1.318 Å	0.004 Å	C–H aver.	0.076	0.005
C(2)–C(3)	1.318 Å	—	C–C	0.041	0.005
C(3)–O(4)	1.375 Å	0.007 Å	C(3)–O(4)	0.050	0.005
O(4)–C(5)	1.427 Å	0.008 Å	O(4)–C(5)	0.054	0.005
C(5)–H(9)	1.10 Å	ass[c]	C(1)–C(5)	0.12	0.02
C(1)–H(6)	1.08 Å	ass	C(2)–C(5)	0.10	0.02
C(3)–H(8)	1.08 Å	ass	C(3)–C(5)	0.060	ass
C(2)–C(3)–O(4)	125.3°	1.2°	C(2)–O(4)	0.060	ass
C(3)–O(4)–C(5)	115.0°	1.2°	C(1)–C(3)	0.052	ass
C(2)–C(1)–H(6)	120°	ass	O(4)–H(9)	0.10	0.01
O(4)–C(5)–H(9)	109.5°	ass	O(4)–H(8)	0.10	—
$\langle\lvert\phi\rvert\rangle$ [a]	23°	6°	all other	0.118	0.027
α [a]	0°	ass			
scale 50 cm	869	14			
scale 25 cm	554	11			
scale 11 cm	347	11			
R[b]	0.1427				
$\Sigma\lvert I_{obs}\rvert$	185030				
$\Sigma w\Delta^2$	43.8×10^5				
$\Sigma\lvert\Delta\rvert$	26500				

[a] See text for explanation of this symbol.

[b] R is defined as $\frac{\Sigma\lvert I_{obs}-I_{calc}\rvert}{\Sigma\lvert I_{obs}\rvert}$.

[c] ass means that this value was assumed and kept constant in the refinements.

tions multiplied by a factor of two, thus roughly removing the effect of correlations between the intensity data[8].

DISCUSSION OF THE STRUCTURE

At room temperature the structure of methyl allenyl ether can well be described by a geometric model with an equilibrium planar *cis*-conformation. (Fig. 1 and Table 2). It has C_s symmetry and there is a large torsional motion around the C(3)–O(4) bond such that the average value of the absolute displacement angle from planarity, $\langle|\phi|\rangle$, is about 23° (stand. dev. 6°). But it should be noted that in this description many torsion dependent framework vibrational amplitudes were constrained at one average value. As they are very much coupled with the torsional motion, their magnitude is not very accurate. However, a refinement with this torsional angle constrained at 0° resulted in a too high average value of 0.16 Å for these framework u values. It also resulted in a slightly less satisfactory agreement between the observed and the calculated intensities (with $R = 0.1472$, $\Sigma w\Delta^2 = 45 \times 10^5$ and $\Sigma|\Delta| = 27200$, compare the data in Table 2). This is most clearly seen in the 3.5 Å region of the radial distribution function (see Fig. 1).

The bond lengths all have expected values when they are compared with those of related molecules like allene[8] or methyl vinyl ether[2]. There is a fairly severe disagreement when the bond angles of the allenyl ether are compared to those of the vinyl ether (in the vinyl ether the angle C–C–O is 123.4°, C–O–C′ is 120.7°). We do not believe that these differences are real, we suspect they are due to the extreme correlation between the conformational angle and the C–O–C′ angle in methyl vinyl ether (Owen and Seip[2]), which makes the magnitude of their angles very uncertain.

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