

An Electron Diffraction Investigation of the Molecular Structure of *trans*-2-Butenedial (Fumaraldehyde) in the Vapour Phase

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Electron diffraction studies of gaseous fumaraldehyde have been carried out. The parameter values were obtained by least squares refinements on the intensity data assuming harmonic vibrations. The molecule is essentially planar with C_{2h} -symmetry. The values obtained for the most important molecular parameters are: C=C, 1.337 Å; C-C, 1.479 Å; C=O, 1.207 Å; C₁-H₁, 1.131 Å; C₂-H₂, 1.094 Å; ∠O=C-C, 123.7°; ∠C=C-C, 122.7°.

The bond distances are given as R_a values.

The structural effects caused by conjugation in an aliphatic molecule have attracted considerable interest during the last few years. It has for example been shown that the length of a carbon-carbon single bond interspaced between two double bonds is clearly dependent on the nature of the second atom in each of the double bonds.^{1,2} In this connection molecules like acrolein,¹⁻³ glyoxal,^{1,2} maleic anhydride,⁴ 1,3-butadiene,^{1,2,5} *cis*⁶ and *trans*⁷ isomers of 1,3,5-hexatriene have been studied. It will be of interest to compare structural parameters for

these molecules with those for *trans*-2-butenedial, where a carbon-carbon double bond is in conjugation with two carbonyl groups. A

Table 1. Fumaraldehyde. Applied force field parameters for calculation of mean amplitudes of vibrations (u values) and perpendicular amplitude correction coefficients (K values). I: Herzberg,¹² II: Fukuyama.¹³

Bond or angle	I	II
Stretching force constants (mdyn/Å)		
C ₁ -H ₁	5.1	3.78
C ₂ -H ₂	5.0	4.64
C-C	4.5	3.46
C=C	9.6	7.14
C=O	12.1	10.3
Bending force constants (mdyn Å/rad ²)		
H-C=C	0.38	0.186
C-C=C	0.70	0.325
H-C-C	0.38	0.259
C ₂ -C ₁ -H ₁	0.38	0.200
H-C=O	0.38	0.375
C-C=O	0.70	0.500
Torsional force constants (mdyn Å/rad ²)		
H-C-C=O	0.09	0.09
H-C-C-H	0.07	0.07
C=C-C-H	0.07	0.07
C=C-C=O	0.12	0.12
H-C=C-H	0.07	0.07
H-C=C-C	0.09	0.09
C-C=C-C	0.12	0.12

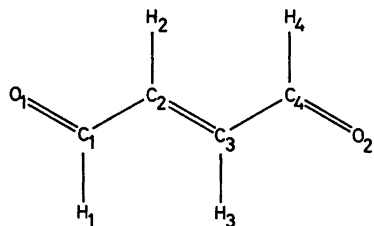


Fig. 1. Fumaraldehyde. Molecular model which shows the numbering of the atoms.

Table 2. Fumarelaldehyde. Observed and calculated mean amplitudes of vibrations (u_{ij}) and calculated perpendicular amplitude correction coefficients (K_{ij}) for distances between carbon and oxygen atoms.^a

Distance	$u_{ij}^{obs.}$	I $u_{ij}^{calc.}$	I K_{ij}	IIa $u_{ij}^{calc.}$	IIa K_{ij}	IIb $u_{ij}^{calc.}$	IIb z_{ij}
C=C	0.0421(25)	0.0406	0.00387	0.0439	0.00492	0.0440	0.00524
C-C	0.0488(10)	0.0488	0.00601	0.0526	0.00801	0.0530	0.00873
C=O	0.0367(7)	0.0374	0.01107	0.0390	0.01353	0.0390	0.01483
C ₁ -H ₁	0.0838(145)	0.0770	0.02713	0.0830	0.03056	0.0830	0.03216
C ₂ -H ₂	0.0825	0.0774	0.01790	0.0789	0.02118	0.0789	0.02177
C ₁ C ₃	0.0625(35)	0.0687	0.00436	0.0858	0.00548	0.0890	0.00598
C ₁ C ₄	0.0691(64)	0.0726	0.00129	0.0881	0.00144	0.0914	0.00154
O ₁ C ₂	0.0548(21)	0.0653	0.01019	0.0731	0.01351	0.0753	0.01496
O ₁ C ₃	0.0705(23)	0.0674	0.00623	0.0800	0.00832	0.0828	0.00922
O ₁ C ₄	0.0831(39)	0.0846	0.00199	0.1027	0.00239	0.1072	0.00263
O ₁ O ₂	0.1052(95)	0.0814	0.00030	0.0949	0.00034	0.0988	0.00036

^a I, and II refer to calculations based on Herzberg's¹² and Fukuyama's¹³ force constants presented in Table 1. IIa and IIb are calculations made for $t = 25^\circ\text{C}$ and $t = 60^\circ\text{C}$ respectively, while I is based on $t = 60^\circ\text{C}$. The numbers in parentheses are standard deviation values as resulting from the least squares analyses.

Table 3. Fumaraldehyde. Structural parameters determined by least squares intensity refinements. The distances are presented as R_a values and the numbers in parentheses are standard deviation values as resulting from the least squares analyses. During the refinements the nonbonded distances were calculated from R_a (I), R_g (II) and R_α (III) parameters.

Distance	I $R_{ij}(\text{\AA})$	I $u_{ij}(\text{\AA})$	II $R_{ij}(\text{\AA})$	II $u_{ij}(\text{\AA})$	III $R_{ij}(\text{\AA})$	III $u_{ij}(\text{\AA})$
C=C	1.3337 (19)	0.0405 (26)	1.3333 (19)	0.0400 (26)	1.3362 (19)	0.0421 (25)
C-C	1.4780 (11)	0.0486 (11)	1.4777 (11)	0.0485 (11)	1.4790 (10)	0.0488 (10)
C=O	1.2068 (10)	0.0357 (9)	1.2069 (10)	0.0355 (10)	1.2067 (10)	0.0367 (7)
C ₁ -H ₁	1.1237 (47)	0.0775 (135)	1.1239 (49)	0.0748 (138)	1.1311 (48)	0.0838 (145)
C ₂ -H ₂	1.0937 (47)		1.0926 (49)		1.0939 (48)	
Angle	($^\circ$)		($^\circ$)		($^\circ$)	
$\angle\text{O=C-C}$	123.20 (0.17)		123.11 (0.17)		123.65 (0.16)	
$\angle\text{C-C=C}$	122.12 (0.23)		122.07 (0.23)		122.73 (0.22)	
$\angle\text{C}_2\text{-C}_1\text{-H}_1$	119.59 (0.69)		119.59 (0.70)		119.51 (0.63)	
$\angle\text{C=C-H}$	124.42 (0.90)		124.27 (0.92)		124.61 (0.80)	
$\sum_i w_i \Delta_i^2$	3.07×10^3 (1.24)		3.22×10^3 (1.30)		2.47×10^3 (1.00)	

similar study of the isomeric *cis*-2-butenedial is also in progress. For the sake of simplicity *trans*-2-butenedial is referred to as fumaraldehyde in this paper. Fig. 1 shows a model of the molecule with the numbering of the atoms that is applied in the present study.

EXPERIMENT AND STRUCTURE ANALYSES

The sample of fumaraldehyde was synthesized from 2,5-dimethoxy-2,5-dihydrofuran by hy-

drolysis.¹⁵ The electron diffraction data were recorded in the usual way with the Oslo apparatus.⁸ The nozzle temperature was $60 - 65^\circ\text{C}$ and the electron wavelength was 0.064584 \AA , corresponding to an accelerating potential of about 36 kV. Photographs were taken at two nozzle-to-plate distances, *i.e.* approximately 48 and 20 cm. Four plates from each distance were selected for use in this investigation. The data were handled in the usual way.⁹ The resulting experimental molecular intensity [$sM(s)$] function extended from $s = 1.625 \text{ \AA}^{-1}$ to $s = 42.0 \text{ \AA}^{-1}$ and is shown in Fig. 2. Two different Δs intervals were used, namely 0.125 \AA^{-1} for

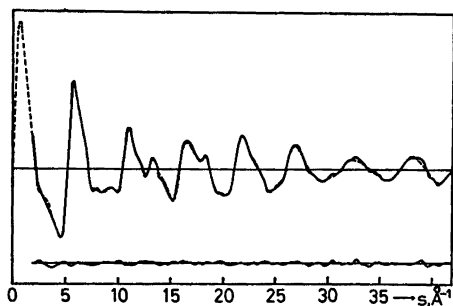


Fig. 2. Fumaraldehyde. Experimental (—) and theoretical (---) molecular intensity functions and the differences between the two.

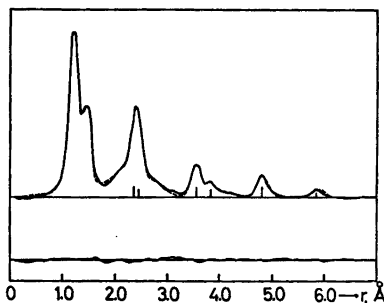


Fig. 3. Fumaraldehyde. Experimental (—) and theoretical (---) radial distribution functions and the differences between the two. Artificial damping constant $k = 0.0015 \text{ \AA}^2$.

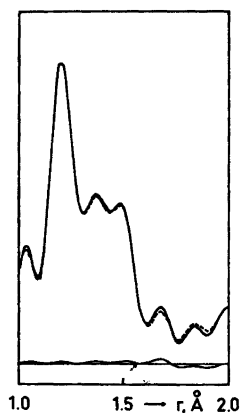


Fig. 4. Fumaraldehyde. Experimental (—) and theoretical (---) sharpened radial distribution functions. Antidamping constant $\alpha = 0.04$.



Fig. 5. Fumaraldehyde. Experimental (—) and theoretical (---) autocorrelation power spectra. Antidamping constant $\alpha = 0.04$. $\tau_{\max} = 30.0 \text{ \AA}^{-1}$.

Table 4. Structural results for fumaraldehyde. The values in parentheses are estimated errors presented as 2.5 times standard deviations from least squares. They include estimates of systematic errors and the effect of correlation.

Distance	R_a (Å)	u (Å)
C=C	1.3362 (45)	0.0421 (60)
C-C	1.4790 (23)	0.0488 (25)
C=O	1.2067 (23)	0.0367 (17)
C ₁ -H ₁	1.1342 (120)	0.0838 (38)
C ₂ -H ₂	1.0939	0.0825
C ₁ ...C ₃	2.4665	0.0625 (88)
C ₁ ...C ₄	3.8321	0.0691 (152)
O ₁ ...C ₂	2.3665	0.0548 (53)
O ₁ ...C ₃	3.5588	0.0705 (58)
O ₁ ...C ₄	4.8153	0.0831 (98)
O ₁ ...O ₂	5.8735	0.1052 (238)
Angle	(°)	
$\angle \text{O}=\text{C}-\text{C}$	123.6 (0.5)	
$\angle \text{C}-\text{C}=\text{C}$	122.7 (0.6)	
$\angle \text{C}_2-\text{C}_1-\text{H}_1$	119.5 (1.6)	
$\angle \text{C}=\text{C}-\text{H}$	124.6 (2.0)	

Table 5. Correlation matrix for

C=C	C-C	C ₁ -H ₁	C=O	∠C-C=C	∠C ₂ C ₁ H ₁	∠O=C-C	∠C=C-H	u(C=C)	
1.000	.449	-.141	.640	-.571	.034	-.352	.091	-.289	
	1.000	-.031	.141	-.469	-.032	-.253	.153	.156	
		1.000	-.322	.102	-.111	.179	-.129	.271	
			1.000	-.352	.095	-.420	.012	-.625	
				1.000	.004	-.267	-.419	.105	
					1.000	-.158	-.330	-.079	
						1.000	.478	.231	
							1.000	.035	
								1.000	
^b	.0019	.0010	.0048	.0010	.22	.63	.16	.80	.0025

^a Distances (R) and root-mean-square amplitudes (u) in Å, angles in degrees. ^b Standard deviations

$s < 10 \text{ \AA}^{-1}$ and 0.250 \AA^{-1} for the large-angle scattering data.

The experimental radial distribution (RD) function obtained by Fourier inversion of the experimental molecular intensity function⁹ is shown in Fig. 3. The large peak centered at 1.2 Å corresponds to the C-H and C=O distances, while the other peak at about 1.4 Å in this overlapping peak complex contains contributions from the carbon-carbon bond distances. The main contributions to the peak with a maximum at about 2.4 Å are from the non-bonded CC and CO distances over one valence angle.

The outer part of the experimental RD function gives information concerning the overall conformation of the molecule. The fairly large and sharp peak at about 5.9 Å is a clear indication that fumaraldehyde is an essentially planar molecule with *s-anti* conformation at the carbon-carbon single bonds. A calculated theoretical RD function with assumed bond distances and valence angles and with an all planar and *anti* conformation supported this observation. The further structure analysis was therefore based on a molecular model with C_{2h} symmetry.

Preliminary values for the bond distances and their mean amplitudes of vibration (u values) were obtained by comparing theoretical and experimental power spectra.^{10,11} The resulting sharpened radial distribution (SRD) and auto-correlation power spectra (APS) functions are shown in Figs 4 and 5.

The molecular structure was determined by least squares analyses of the molecular intensity function. During this process the dependent non-bonded distances are calculated from the independent geometrical parameters (bond distances, valence and dihedral angles), and it is also necessary to calculate the partial derivatives of the nonbonded distances with respect to the various independent geometrical parameters. It is of importance to define which type of inter-nuclear distance is used as basis for calculation of dependent nonbonded distances. Electron diffraction structural results are usually presented in the form of R_a , R_g or R_α structures.¹² The following approximate relationships exist between the different R values:

$$R_a \simeq R_g - u^2/R \simeq R_\alpha + K - u^2/R$$

where u is the mean amplitude of vibration and K is the perpendicular amplitude correction coefficient.

R_α gives the distance between average positions of two atoms and an R_α structures is therefore geometrically consistent. This is not true for R_a and R_g structures where shrinkage effects might be observed.¹²

Based on an electron diffraction experiment the interatomic distances may be obtained as R_a or R_g values. R_α parameters are not directly accessible since the K values can not be experimentally obtained by this method. It is,

parameters of fumaraldehyde.^a

$u(\text{C}-\text{C})$	$u(\text{C}_1\text{H}_1)$	$u(\text{C}=\text{O})$	$u(\text{O}_1\text{O}_2)$	$u(\text{O}_1\text{C}_2)$	$u(\text{O}_1\text{C}_3)$	$u(\text{O}_1\text{C}_4)$	$u(\text{C}_1\text{C}_3)$	$u(\text{C}_1\text{C}_4)$
-.291	-.492	-.094	-.001	-.033	.002	-.001	-.052	-.026
.059	-.036	.172	.007	.089	.045	.032	.109	-.012
.045	.311	.188	-.032	-.120	-.080	-.070	-.055	-.027
-.390	-.872	-.447	-.014	-.085	-.042	-.033	-.121	-.009
.116	.225	.004	.007	-.529	.034	-.018	-.501	.012
-.030	-.065	-.032	-.002	.108	.000	-.055	-.059	.084
.160	.373	.181	.001	.574	-.008	.015	.770	-.064
.042	.013	.067	-.011	.486	.043	.046	.596	-.151
.627	.642	.741	.013	.103	.051	.038	.131	.002
1.000	.404	.513	.016	.118	.055	.042	.123	.012
	1.000	.500	.024	.115	.063	.046	.148	.001
		1.000	.024	.145	.076	.055	.157	-.002
			1.000	.011	.026	.050	.009	-.007
				1.000	.027	.040	.704	-.032
					1.000	.021	.034	-.124
						1.000	.040	.006
							1.000	-.074
								1.000
.0010	.0015	.0007	.0086	.0019	.0022	.0036	.0046	.0047

from least squares.

however, possible to calculate the shrinkage corrections (); transformation to R_α parameters) from a simplified force field.^{17,18}

In the present study two sets of u and K values were calculated, based on Herzberg's¹² and Fukuyama's¹³ force constants, respectively. The force constants are shown in Table 1, while the calculated mean amplitudes and perpendicular correction coefficients for the most important interatomic distances are presented in Table 2. The calculations based on Fukuyama's force constants were carried out for $t=25^\circ\text{C}$ and $t=60^\circ\text{C}$ in order to study the influence of the temperature on the results, while the temperature was set equal to 60°C when Herzberg's force constants were applied. In accordance with expectations the u and K values based on Herzberg's fairly large force constants are generally smaller than those based on Fukuyama's force constants.

The least squares analyses were carried through for R_a , R_g and R_α structures. It was possible to determine all the mean vibrational amplitudes experimentally except for some of the nonbonded oxygen-hydrogen distances. In calculation of R_α structures the experimental u values were applied together with the calculated K values. The K values based on Fukuyama's force constants (II) gave clearly the best R_α structure. The results for $t=60^\circ\text{C}$ were also better than those for $t=25^\circ\text{C}$, as might be expected since the experimental data were recorded at $t=60-65^\circ\text{C}$.

Table 3 shows the results based on R_a (I), R_g (II) and R_α (III) structures. The squared error sum and the standard deviation values for the determined parameters are smallest when an R_α structure is determined. These results show, hardly surprisingly, that in an electron diffraction study of a molecule with a long skeleton, like the present case, refinements including shrinkage corrections are superior to those without such corrections.

Least squares refinements without shrinkage corrections (I and II) might be expected to give slightly smaller values for the $\text{C}=\text{C}$, $\text{C}-\text{C}$ and $\text{C}=\text{O}$ bond distances and for the $\text{O}=\text{C}-\text{C}$ and $\text{C}=\text{C}-\text{C}$ valence angles. From Table 3 small effects in the expected direction will be noted for all the discussed parameters except for the $\text{C}=\text{O}$ bond, where there is practically no difference between the three results.

The final structural parameters for fumaraldehyde are presented in Table 4. The results are obtained by a least squares analysis based on an R_α structure. The correlation matrix for the parameters of fumaraldehyde is presented in Table 5 and is based on refinements where the most important non-bonded distances are included as parameters. The theoretical molecular intensity function calculated from the parameters presented in Table 4 is shown in Fig. 2 together with the experimental $sM(s)$ function. The corresponding radial distribution functions are shown in Fig. 3.

Table 6. Comparison of the bond distances obtained for fumaraldehyde with results obtained for similar molecules studied by gas electron diffraction. The distances are given in Å as R_g values.

Molecule	$C_{sp^2}-C_{sp^2}$	C=C	C=O	C-H _{ole.}	C-H _{ald.}	Ref.
Fumaraldehyde	1.479	1.336	1.207	1.094	1.134	^c
<i>trans</i> -3-Hexene-2,5-dione	1.490	1.329	1.211			14
Acrolein	1.478	1.335	1.208	1.094	1.123 ^a	1
	1.481	1.340	1.209	1.079	1.099	3
1,3-Butadiene	1.463	1.341		1.090		1
	1.467	1.344		1.094		5
<i>trans</i> -1,3,5-Hexatriene	1.458	1.337 (terminal)		1.104		7
		1.368 (central)				
<i>cis</i> -1,3,5-Hexatriene	1.462	1.336 (terminal)		1.090		6
		1.362 (central)				
Glyoxal	1.525		1.207		1.116	1
Maleic anhydride	1.500 ^b	1.330 ^{a,b}	1.195 ^b	1.091 ^b		4
Propynal			1.214 ^b		1.130 ^b	23

^a Not independently determined. ^b Given as R_g value. ^c Present study.

Table 7. Comparison of bond angles obtained for fumaraldehyde with results obtained for similar molecules studied by gas electron diffraction.

Molecule	$\angle C=C-C$ (°)	$\angle C-C=O$ (°)	$\angle C=C-H$ (°)	$\angle H-C=O$ (°)	Ref.
Fumaraldehyde	122.7	123.6	124.6	116.9	^a
<i>trans</i> -3-Hexene-2,5-dione	122.4	121.7	124.0		14
Acrolein	120.3	123.3	121.3	122.3	1
	119.9		121.6		3
1,3-Butadiene	123.3		121.8 ^d		1
	122.8		119.5		5
<i>trans</i> -1,3,5-Hexatriene	124.4 ^b		115.0 ^e		7
	121.7 ^c				
<i>cis</i> -1,3,5-Hexatriene	125.9 ^b		118.0 ^e		6
	122.1 ^c				
Glyoxal		121.2		126.6	1
Propynal		124.2		122.1	23

^a Present study. ^b The angle involving central C=C. ^c The angle involving terminal C=C. ^d Average value. ^e Not independently determined.

DISCUSSION

In Table 5 the bond distances of fumaraldehyde are compared with results obtained for other similar molecules, studied by gas electron diffraction.

The secondary environment effect of oxygen on the C-C bond distances that was pointed out by Kuchitsu *et al.*¹ is nicely reproduced in the present study. The C-C bond distance is significantly larger than in conjugated hydro-

carbons like 1,3-butadiene and is found to be approximately the same as in acrolein and *trans*-3-hexene-2,5-dione¹⁴ where the C-C bonds have similar environments.

If a C-C single bond in a conjugated system is shortened by conjugation, the double bonds in such a system might be expected to increase. The changes are, however, expected to be much smaller for multiple bonds¹⁸⁻²¹ and very few experimental data exist that significantly confirm such multiple bond shortenings. In the

present case the C=C and C=O bond lengths are found to be in good agreement with results obtained for other similar conjugated molecules.

It is generally more difficult to determine C-H bond distances and C-C-H valence angles accurately by electron diffraction than those involving heavier atoms, as hydrogen is a relatively weak scatterer of electrons. Bond distances and angles involving hydrogen also have the largest vibrational effects, and the differences among the structural parameters under different definitions are the largest. This is demonstrated for the C-H bond distances in Tables 3 and 4.

The C-H bond distances determined for fumaraldehyde are in good agreement with the other data presented in Table 5. Normally a C-H bond in an aldehyde group is found to be about 0.03 Å longer than a vinylic C-H bond, in general agreement with the result obtained in the present study.

The valence angles between the heavier atoms are in accordance with the other structural results listed in Table 6. The valence angles involving hydrogen deviate considerably from some of the other results in Table 6. It should be noted that the C=C-H angle (124.6°) is found to be larger and the H-C=O (116.9°) angle to be smaller than expected. There is, however, a high degree of coupling between these two parameters. Because of the general uncertainty in valence angles involving hydrogen atoms these discrepancies are probably not important and will not be discussed further.

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