The Molecular Structure of Acetaldehyde

BY D. P. STEVENSON,[1] H. D. BURNHAM AND VERNER SCHOMAKER

Ackermann and Mayer[2] investigated the structure of acetaldehyde by the electron diffraction technique using 6.4 kilovolt electrons. Their photographs showed only two maxima and one minimum; hence it was necessary for them to assign very large uncertainties to their results. Since the distances they reported were considerably shorter than predicted by the covalent radius table,[3] it was decided that the structure of acetaldehyde should be reinvestigated using fast electrons.

Experimental.—Acetaldehyde was obtained by the acid depolymerization of Eastman Kodak Co. paraldehyde and also from a 95% solution of acetaldehyde in water (Eastman). In each case the acetaldehyde was distilled several times *in vacuo*, generous first and last fractions being discarded. From the purified liquid the vapor was allowed to expand into a carefully evacuated bulb which could be attached to the apparatus by means of a ground joint. In order to obtain completely satisfactory photographs, it was found necessary to have the vapor pressure in the sample bulb close to one atmosphere.

The Pasadena apparatus has been described by Brockway.[4a] The Princeton apparatus is similar to the Pasadena apparatus and has been used in other research.[4b] The wave length of the electrons was determined from transmission photographs of gold foil ($a = 4.070$ Å.), and it was approximately equal to 0.06 Å. for both the Pasadena and the Princeton photographs.

Interpretation.—Since the Pasadena and the Princeton photographs are identical both qualitatively and quantitatively, they will not be discussed separately.

The photographs showed six measurable maxima and minima. Two shelves were also present, the first preceding the first minimum and the second following the fifth maximum. They will be designated by the letters *A* and *B*, respectively. The fifth maximum and feature *B* resemble the maximum and shelf which appear on carbon dioxide photographs at the same value of s.[5] For the visual comparison of the photographs with the

theoretical intensity curves, the most important characteristics of the photographs are that (1) the third minimum is deeper than either the second or fourth minimum, and (2) the third maximum is stronger than the fourth maximum. The measured s $\left(s_0 = \frac{4\pi}{\lambda} \sin \frac{\vartheta}{2}\right)$ values of the maxima and minima are given in the fifth column of Table I.

A radial distribution function[6] was calculated using the positions of both the maxima and minima. The coefficients were determined according to the method recommended by Schomaker.[7] These coefficients and the visually estimated intensities are given in columns 3 and 4 of Table I.

$$R(d) = \Sigma_n C_n \frac{\sin d\, s_n}{d\, s_n} \qquad C_n = f(I_0, s_n) \qquad (1)$$

A plot of $R(d)$ against d is shown in Fig. 1. The maxima at 1.21, 1.51, and 2.33 Å. correspond to the carbon–oxygen and carbon–carbon bond distances and the non-bonded carbon–oxygen distance, respectively.

TABLE I

Max.	Min.	C_n	I_0	s_0	$s^a_{calcd.}$	s_c/s_0
A			2	3.59	...	...
	1	– 9	–12	4.35	4.05	$(0.931)^b$
1		14	12	6.23	5.88	$(0.944)^b$
	2	– 2	– 4	7.45	7.60	$(1.020)^b$
2		10	8	8.73	8.42	0.964
	3	– 7	– 6	9.86	9.60	.974
3		4	4	11.26	11.20	.995
	4	– 2	– 2	12.36	12.18	.985
4		2	2	13.73	13.10	$(.954)^b$
	5	– 8	– 6	15.12	14.70	.972
5		10	6	16.75	16.40	.979
B				...	...	...
	6	– 2	– 3	20.02	19.52	.975
6		3	3	21.91	21.30	.972
Average of 8 features						.977 ± 0.007

^{a} From curve with $\rho = 1.25/1.54$, $\alpha = 121.6°$. ^{b} Omitted from average because of difficulty of measurement

$$\text{C–C} = 1.54 \times 0.977 = 1.504 \text{ Å.}$$
$$\text{C–O} = 1.25 \times .977 = 1.222 \text{ Å.}$$
$$\text{C–O} = 2.44 \times .977 = 2.384 \text{ Å.}$$

The qualitative appearance of the theoretical intensity curves for acetaldehyde is dependent on two parameters, ρ, the ratio of the carbon–oxygen

(1) National Research Fellow.

(2) P. G. Ackermann and J. E. Mayer, *J. Chem. Phys.*, **4**, 377 (1936).

(3) L. Pauling and M. L. Huggins, *Z. Krist.*, **87**, 205 (1934); L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 1223 (1937).

(4) (a) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936); (b) J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

(5) Verner Schomaker and D. P. Stevenson, THIS JOURNAL, to be published.

(6) L. Pauling and L. O. Brockway, *ibid.*, **57**, 2684 (1935).

(7) Verner Schomaker, American Chemical Society meeting, Baltimore, Md., April, 1939.
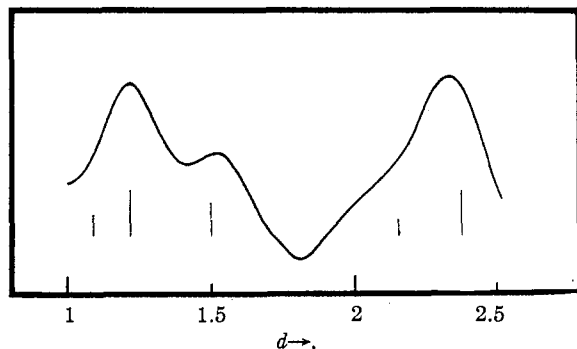
Fig. 1.—Radial distribution function, $R(d)$.

to carbon–carbon distance, and α, the carbon–carbon–oxygen angle. It was assumed that the hydrogen–carbon distance is equal to its value in methane, 1.09 Å., and that the configuration of the methyl group is tetrahedral.

In calculating the theoretical intensity curves it was found necessary to include temperature factors[4a] in the coefficients of the terms involving hydrogen–carbon distances as well as to take into account the effectively larger atomic scattering factor for electrons, $(Z - f)$, of hydrogen,[8] as compared with carbon and oxygen. The modified simple intensity formula thus had the following form

$$I(s) = 6\,\frac{\sin 1.54s}{1.54s} + 3.75\,\frac{\sin 1.09s}{1.09s}\,e^{-a_1s_2}$$

$$+ 3.75\,\frac{\sin 2.16s}{2.16s}\,e^{-a_1s_2} + 8\,\frac{\sin\,(C\text{–}O)s}{(C\text{–}O)s}$$

$$+ 8\,\frac{\sin\,(C\text{–}O)s}{(C\text{–}O)s}$$

$$a_1 = 0.0022,\quad a_2 = 0.0043 \quad (2)$$

The a's are equal to half the mean square of the change in the distance between the hydrogen and the carbon atoms due to the vibrations of the molecule. They were evaluated from the known stretching and bending frequencies of ethane. The method used in their calculation will be discussed in detail by one of us.

It was further found that the terms involving the methyl–hydrogen to oxygen distances and the

(8) L. Pauling and J. Sherman, Z. Krist., **81**, 1 (1932).

carbonyl–hydrogen distances could be omitted from the intensity formula without affecting its form or the positions of its maxima or minima.

Nineteen curves were calculated using equation (2). Some of these are shown in Fig. 2. The parameter ρ was varied from 1.30/1.54 to 1.22/1.54 and α from 112 to 127°. All models with ρ greater than 1.26/1.54 could be eliminated because for them the second minimum is deeper than the third and because feature B appears as a small maximum closer to the sixth than to the fifth maximum. For ρ less than 1.24/1.54 and α greater than 123°, the curves are unsatisfactory because the fourth minimum is too shallow and feature B does not have the appearance it has on
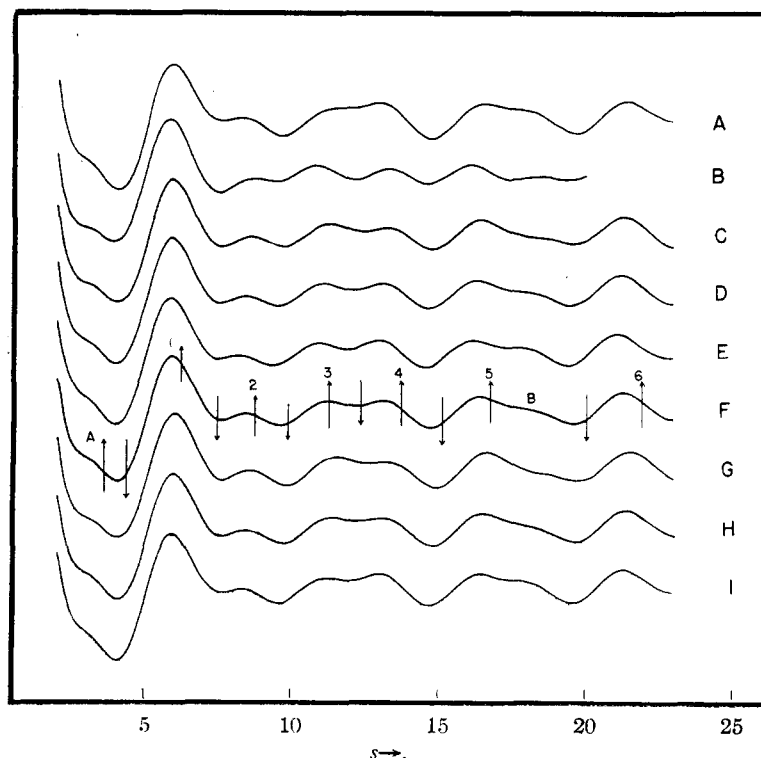

Fig. 2.—Theoretical intensity curves:

Curve A	$\rho = 1.22/1.54,\ \alpha = 121.6°$
Curve B	$\rho = 1.30/1.54,\ \alpha = 121.6°$
Curve C	$\rho = 1.26/1.54,\ \alpha = 119.3°$
Curve D	$\rho = 1.26/1.54,\ \alpha = 121.6°$
Curve E	$\rho = 1.26/1.54,\ \alpha = 124.5°$
Curve F	$\rho = 1.25/1.54,\ \alpha = 121.6°$
Curve G	$\rho = 1.24/1.54,\ \alpha = 119.3°$
Curve H	$\rho = 1.24/1.54,\ \alpha = 121.6°$
Curve I	$\rho = 1.24/1.54,\ \alpha = 124.5°$

the photographs. The curves calculated with α less than 119° and all values of ρ may be eliminated because feature B does not appear. Curves for α greater than 123° are unsatisfactory because

B is too pronounced, appearing as a maximum rather than as a shelf following the fifth maximum. The curves calculated for $1.26/1.54 \geq \rho \geq 1.24/1.54$ and $119° \leq \alpha \leq 123°$ are qualitatively satisfactory. Quantitative comparison of the photographs with the curves calculated within the satisfactory ranges of ρ and α all give 1.22 Å. for the carbon–oxygen bond distance, 2.38 Å. for the non-bonded carbon–oxygen distance, and from 1.49 to 1.51 Å. for the carbon–carbon distance. Column 7, Table I gives a typical example of this comparison. Although the model with $\rho = 1.22/1.54$ and $\alpha = 119.3°$ cannot be eliminated, its curve is not so satisfactory as the curves for models with larger values of ρ inasmuch as the fourth minimum is too shallow and the fourth maximum is too weak.
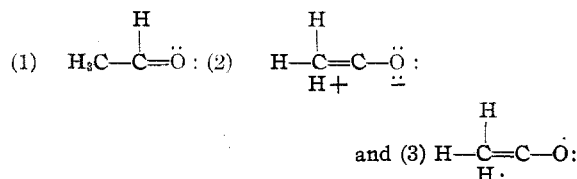
Our final results for the structure are C–C = 1.50 ± 0.02 Å., C–O = 1.22 ± 0.01 Å., C–O = 2.38 ± 0.01 Å., C–H = 1.09 Å. (assumed), and the angle C–C–O = 121 ± 2°.

Discussion.—In a recent communication[9] it was reported that the carbon–oxygen distance in formaldehyde is 1.21 ± 0.01 Å. and this distance has been found to be 1.20 ± 0.02 Å.[10] in glyoxal; thus, with our results for acetaldehyde there are three determinations of the length of the carbon–oxygen double bond giving an average of 1.21 ± 0.02 Å.

Infrared and Raman spectra[11] studies of allene and ethylene yield 1.330 Å. for the length of the carbon–carbon double bond. This value has been confirmed recently by a new electron diffraction investigation of ethylene.[12] Thus, taking the carbon–carbon distances as standards, the subtrahend in Pauling's[13] rule for obtaining double bond distances from single bond distances is $1.540^{14} - 1.330 = 0.21$ Å. The carbon–oxygen single bond distance has been found to be 1.42 ± 0.02 Å. in dimethyl ether,[4a] t-butyl alcohol,[15] and cis-butene oxide,[4a] 1.43 ± 0.02 Å. in paraldehyde[4a] and $trans$-butene oxide,[4a] 1.44 ± 0.02 Å. in α-methylhydroxylamine,[4a] 1.46 ± 0.04 Å. in 1,4-dioxane,[4a] and 1.41 ± 0.02 Å. in methyl alcohol.[5]

(9) D. P. Stevenson, J. E. LuValle and V. Schomaker, THIS JOURNAL, **61**, 2508 (1939).
(10) J. E. LuValle and V. Schomaker, to be published.
(11) E. H. Eyster, *J. Chem. Phys.*, **6**, 580 (1939).
(12) V. Schomaker, to be published.
(13) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 159.
(14) The carbon–carbon distance in diamond; *cf.* "Strukturbericht."
(15) J. Y. Beach and D. P. Stevenson, THIS JOURNAL, to be published.

Taking 1.42 Å. as the most likely value for the carbon–oxygen single bond distance (small weight may be attached to values found in the cyclic molecules since their complexity makes reliable determination of individual distances exceedingly difficult), the expected carbon–oxygen double bond distance becomes $1.42 - 0.21 = 1.21$ Å., in exact agreement with the average found from formaldehyde, glyoxal, and acetaldehyde.

The shortening of the carbon–carbon distance to 1.50 Å. from the covalent value of 1.54 Å. is probably due in part to resonance of the type suggested by Pauling, Springall, and Palmer,[16] for methylacetylene and methyl cyanide, the resonating structures being

$$
(1) \quad H_3C\!-\!\overset{\displaystyle H}{\underset{\displaystyle |}{C}}\!=\!\ddot{O}: \quad (2) \quad H\!-\!\overset{\displaystyle H}{\underset{\displaystyle |}{\underset{\displaystyle H+}{C}}}\!=\!C\!-\!\overset{..}{\underset{..}{O}}:
$$

$$
\text{and } (3) \quad H\!-\!\overset{\displaystyle H}{\underset{\displaystyle |}{\underset{\displaystyle H\cdot}{C}}}\!=\!C\!-\!\ddot{O}:
$$

and in part to the formal charge effect,[17] resulting from resonance with

$$
(4) \quad H_3C\!-\!\overset{\displaystyle H}{\underset{\displaystyle |}{\underset{\displaystyle +}{C}}}\!-\!\overset{..}{\underset{..}{O}}:^{18}
$$
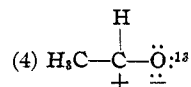
However, it is difficult to estimate the relative contributions of the double bond character and of the formal charge.

If the increase of the R–C–O bond angle in going from formaldehyde[9] (120°) to acetaldehyde (121°) is real, it may be interpreted as indicating a greater amount of p orbital in the carbon–carbon bond than there is in the corresponding carbon–hydrogen bond.

The agreement with our values of the results of Ackermann and Mayer,[2] C–C = 1.51 ± 0.05 Å., C–O = 1.20 ± 0.05 Å., and the angle C–C–O = 122 ± 5° is remarkable inasmuch as Ackermann and Mayer determined the three parameters from but three measurements.

Summary

From electron diffraction photographs of acetaldehyde the value 1.50 ± 0.02 Å. has been found for the carbon–carbon distance, 1.22 ± 0.02 Å. for the carbon–oxygen distance, and 121 ± 2° for the carbon–carbon–oxygen angle. It is suggested that in general the covalent carbon–

(16) L. Pauling, H. D. Springall and K. J. Palmer, *ibid.*, **61**, 927 (1939).
(17) N. Elliott, *ibid.*, **59**, 1380 (1937).

oxygen double bond distance is about 1.21 Å. instead of 1.24 Å. The structure of acetaldehyde is discussed briefly in terms of resonance among several valence-bond structures.

The Heat of Combustion of *cis*- and *trans*-Azobenzene[1]

BY R. J. CORRUCCINI AND E. C. GILBERT

In making theoretical calculations of bond energies, Pauling[2] called attention to the unsatisfactory character of the data on the heat of combustion of azobenzene, and a redetermination of this quantity was undertaken in this Laboratory. While the investigation was still in the early stages, Hartley[3a] reported the preparation of the compound in the two isomeric forms, *cis*- and *trans*-, theoretically to be expected but previously never isolated. The two forms exist in equilibrium in solution, transition to the *cis* form being favored by sunlight. In the solid form the *cis* isomer is reported to be stable. In all previous work with azobenzene, therefore, the possibility exists that undetermined percentages of the two forms may have been present.

With this knowledge at hand the standard methods of purification were modified to take advantage of Hartley's findings in order that the two separate isomers might be prepared in the pure state, and the heat of combustion determined for each. In addition these results permit a new approach to the determination of the heat of transition, which has been measured by Hartley[3b] by another method.

The Calorimeter.—The calorimeter system and its calibration have been described previously in detail.[4] The heat of combustion of the *trans* isomer was measured before certain structural changes had been made in the system and hence the energy equivalent was somewhat different from that described in the reference cited. At the time of the work on *trans*-azobenzene the energy equivalent of the calorimeter (without the charge) was found to be 2507.6, 2507.5, 2506.9

(2505.4), 2507.9, 2507.1, with a mean value of 2507.4 ± 0.4 cal. deg.$^{-1}$. For the combustion of *cis*-azobenzene the calorimeter equivalent was that for which details are given,[4] 2550.0 ± 0.2 cal. deg.$^{-1}$.

The results of this paper are given in conventional calories calculated from international joules by dividing by the factor 4.1833[5] and are referred to the standard temperature of 25° in the same manner as previously.[4]

Preparation of Compounds.—Hartley[3] has shown that the formation of the *cis* form is favored by solar radiation, and that, being more polar, this form is consequently more soluble in polar solvents, this preferential solubility being the basis of the separation of the two forms.

Various samples of azobenzene were therefore recrystallized from aqueous ethanol and methanol, and from benzene and chloroform, all in very dim light. All the samples melted at 68.0–68.1° (by the capillary tube method) against a thermometer calibrated by the Bureau of Standards, and were combined for a final recrystallization from aqueous acetone. Any possible small amount of the *cis* form present originally should have been converted due to the temperature effect, or left in solution, it being thirty times as soluble in water as the *trans*-azobenzene. The product was dried in the dark over phosphorus pentoxide and melted at 68.1°. The minimum time for drying of these samples before combustion was eight days.

For the preparation of *cis*-azobenzene the most recent method of Hartley was used.[3b] A saturated solution of azobenzene in glacial acetic acid (500 cc.) was insolated for several hours in bright sunlight, keeping it in an ice-bath to reduce the temperature. This precaution was found to be imperative though not mentioned by Hartley. From this point all operations were carried out in the darkroom. Four hundred fifty cc. of water was added to precipitate the major portion of the *trans*-azobenzene and the solution filtered. The filtrate was diluted further with 500 cc. of water and extracted with chloroform. The extract was washed with water and evaporated immediately with reduced pressure. The products from several exposures were united and recrystallized twice more from petroleum ether (b. p. 40–60°) at temperatures from 20 to −10°, each time being washed with liberal portions of the solvent. The melting point of the compound measured by the "dip" method used by Hartley was 71.6°, slightly above the m. p. (71.4°), previously reported for the substance. The

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(2) Pauling, THIS JOURNAL, **54**, 3570 (1932).

(3) (a) Hartley, *Nature*, **140**, 281 (1937); (b) *J. Chem. Soc.*, 633 (1938).

(4) Hughes, Corruccini and Gilbert, THIS JOURNAL, **61**, 2639 (1939).

(5) Rossini, *Chem. Rev.*, **18**, 233 (1936).