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Electron Diffraction Investigation of the Molecular Structure of Thioacetic Acid

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The structure of thioacetic acid has been investigated by the method of electron diffraction. The molecule was found to have very little resonance interaction between bonds. The interatomic distances found are: $C=O = 1.24 \pm 0.04$A; $C-S = 1.78 \pm 0.02$A; $C-C = 1.54 \pm 0.06$A. The angle CCO was found to be $125° \pm 5°$ and angle CCS, $110° \pm 5°$. The distances assumed are: $C-H = 1.09$A and $S-H = 1.34$A. Angle OCS was assumed to be $125°$.

THE structure of thioacetic acid in the vapor state has been investigated through its electron diffraction patterns. High speed electrons, of wave-length 0.0615A, were employed. This substance gave good electron diffraction pictures which showed ten measurable rings. Measurements were made of ten different photographs. A description of the electron diffraction technique and of the instrument used for the present investigation has been made by Brockway.[1]

The values of $q_{obs.}$, listed in Table I, were obtained from the scattering angle and electron wave-lengths by use of the relation,

$$q = 40/\lambda(\sin \phi/2).$$

Two radial distribution curves were made using the formula,

$$lD(l) = \sum_k C_k \sin \frac{\pi}{10} q_k l,$$

and the Schomaker method[2] of estimating intensities. In one the C_k's were used as the estimated intensities of the maxima and minima of the rings multiplied by the damping factor, $\exp(-aq^2)$. The other was a radial integral made from a curve drawn to represent the scattering pattern of the molecules as nearly as it could be estimated from the pictures. The intensities were read from this curve at intervals of $0.05q$ and were multiplied by a damping factor, $\exp(-aq^2)$, to obtain the intensity constants, C_k's, in the above equation. The two radial distribution curves agree in that the essential peaks come in the same places on each. The radial integral curve shown in Fig. 1 is the only one given here.
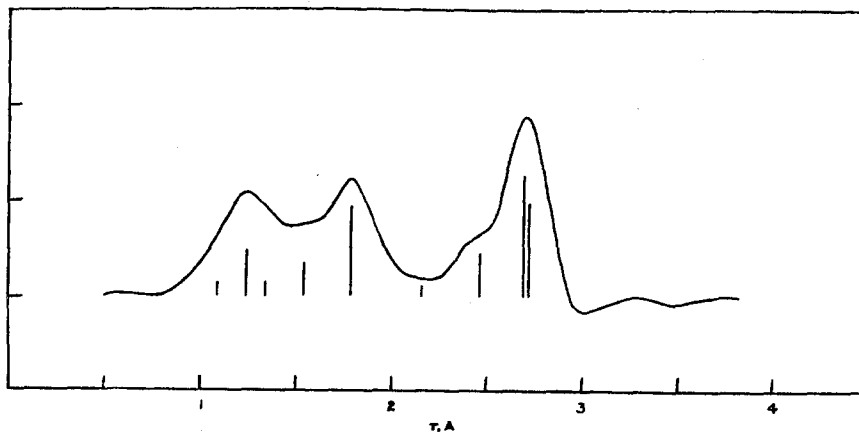

FIG. 1. Radial distribution curve for thioacetic acid. Bars are for Model *A* of Table II.

[1] L. O. Brockway, Rev. Mod. Phys. 8, 231 (1936).
[2] V. Schomaker, American Chemical Society Meeting, Baltimore, Maryland, April, 1939.

Theoretical intensity curves for several models were plotted (Fig. 2), using the formula,

$$I(q) = \sum_i \sum_j (Z_i Z_j / l_{ij}) \sin \frac{\pi}{10} q l_{ij}.$$

In these the scattering factors are assumed to be proportional to the atomic numbers of the atoms. For the terms containing hydrogen, temperature corrections were applied.[3]

All calculations were made with International Business Machines.

DISCUSSION OF RESULTS

In interpretation of results the following assumptions were made: C–H distances were taken as 1.09A, and S–H ones as 1.34A; angle SCO was assumed to be 125°; all atoms of the molecules except those of hydrogen were considered in a single plane. A certain amount of resonance might be anticipated between the C–S and C=O. Such interation, however, would be unlikely to affect measurably angle SCO. As the C–S bond takes on double bond character, the C=O bond correspondingly approaches a single bond. This would tend to keep the bond angle constant and to keep the bonds to the central carbon coplanar.

In the radial distribution curve there are three well-defined peaks, at 1.24A, 1.78A, and 2.70A, respectively; one not completely resolved occurs at about 2.44A. Those at 1.24A and 1.78A can be identified with the C=O and C–S distances, respectively. The peak at 2.70A, strong and rather sharp, is assumed to be due to the non-bonded S–O and S–C scattering terms which are too close together to be separated. The peak at about 2.44A may be identified with the non-bonded C–O scattering. The C–C term, because of its low scattering power and because of its occurrence between the strong peaks at 1.24A and 1.78A, is not resolved.

Of the several models listed in Table II, Model A is the one suggested by the peaks of

[3] D. P. Stevenson, H. D. Burnham, and V. Schomaker, J. Am. Chem. Soc. 61, 2922 (1939).
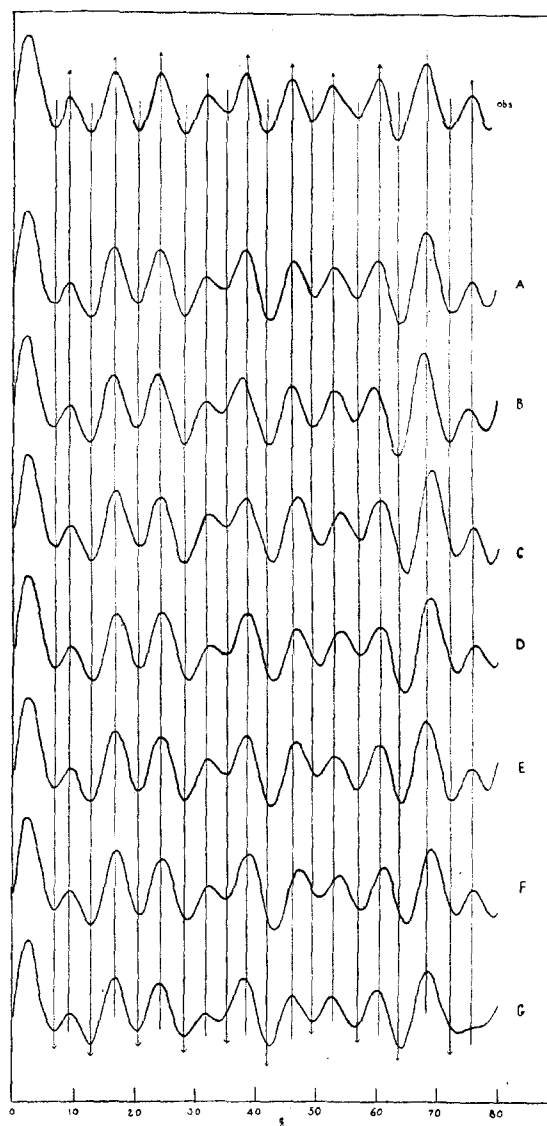
FIG. 2. Curve (marked obs.) drawn to represent the appearance of diffraction pictures, and theoretical scattering curves for models listed in Table II.

the radial distribution curve. The other models, for which the distances vary as much as 0.03A from those of Model A, produce slightly less satisfactory agreement than does Model A with the observed scattering curve as well as with the radial distribution curve. The values for the various parameters are thus determined as: C=O = 1.24±0.04A; C–S = 1.78±0.02A; C–C = 1.54 ±0.06A; angle CCS = 110°±5°; angle CCO

TABLE I. Electron diffraction data for thioacetic acid.

Max.	Min.	I	C	$q_{obs.}$	$q_{calc.}$[a]	$q_{calc.}/q_{obs.}$
	1	-8	-80	7.05	6.95	0.986
1		3	30	9.28	9.30	1.002
	2	-10	-92	12.99	12.90	0.993
2		10	87	16.83	16.80	0.998
	3	-9	-73	20.71	20.70	1.000
3		10	75	24.31	24.30	1.000
	4	-9	-61	28.33	28.40	1.002
4		3	20	31.84	32.00	1.005
	5	-3	-16	35.39	35.00	0.989
5		10	48	38.58	38.40	0.995
	6	-10	-42	41.88	42.50	1.015
6		8	28	46.12	46.50	1.008
	7	-6	-24	49.37	49.95	1.012
7		6	16	52.90	53.30	1.008
	8	-5	-10	57.03	57.00	0.999
8		8	13	60.56	60.50	0.999
	9	-12	-16	63.59	64.10	1.008
9		12	12	68.36	68.40	1.001
	10	-8	-6	72.17	72.75	1.008
10		4	2	75.90	75.75	0.998

Average 1.001
Average deviation 0.006

[a] For Model A of Table I.

TABLE II. Distances and bond angles for thioacetic acid models.

Model	$C=O$	$C-C$	$C-S$	Angle OCS	Angle CCO	Angle CCS	Average deviation of $q_{calc.}$ from $q_{obs.}$
A	1.24A	1.54A	1.78A	125°	125°	110°	0.006
B	1.24	1.54	1.81	125°	125°	110°	0.015
C	1.24	1.48	1.78	125°	125°	110°	0.014
D	1.21	1.54	1.78	125°	125°	110°	0.012
E	1.27	1.54	1.78	125°	125°	110°	0.012
F	1.24	1.54	1.75	125°	125°	110°	0.015
G	1.24	1.54	1.78	125°	121°	114°	0.017

$= 125° \pm 5°$; angle OCS $= 125°$ (assumed). Though the photographs were excellent and Model A agrees closely with the observed features of the rings, the bond distances and angles could not be determined with great accuracy because none of the qualitative features of the computed curves are particularly sensitive to variations of the parameters in the neighborhood of the chosen values.

From a consideration of resonance effects in other molecules, a small amount of double bond character would be expected to shorten measurably the $C-S$ bond distance. The fact that the $C-S$ distance, 1.78A, found for this molecule is only slightly less than the sum of the single bond covalent radii of S and C, 1.81A, indicates that there is very little resonance of the $C-S$ bond with the carbonyl group. The amount of double bond character of $C-S$ computed from the observed distance using Pauling's rule[4] is only six percent. In contrast, similar compounds in which the S is replaced by the more electronegative N and O atoms, the amides or esters for example, show appreciable interaction[5] with the $C=O$.

The author is indebted to Professor Linus Pauling for his helpful advice, also to Doctor Verner Schomaker and Doctor Robert Spurr for their assistance.

[4] Linus Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939), p. 164.
[5] Linus Pauling, reference 4, p. 130.