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The Molecular Structure of Thioxanthone as Studied by Gas Phase Electron Diffraction

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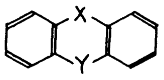
The molecular structure of thioxanthone has been determined from gas electron-diffraction data. The molecular parameter values and their uncertainties are $r_g(\mathrm{C{-}C})=1.401\pm0.001$ Å, $r_g(\mathrm{C{-}H})=1.099\pm0.007$ Å, $r_g(\mathrm{C{-}S})=1.751\pm0.002$ Å, $r_g(\mathrm{C{-}C_c})=1.498\pm0.004$ Å, $r_g(\mathrm{C_c{-}O})=1.232\pm0.006$ Å, $\angle\mathrm{CSC}=103.4\pm0.3°$, $\angle\mathrm{CC_cC}=119.4\pm0.6°$, and θ(dihedral angle)$=169.0\pm1.6°$, where the angle parameters are r_α parameters. The dihedral angle of thioxanthone is much larger than those of related molecules.

The crystal structure studies of heterocyclic molecules such as type **1** have revealed that the dihedral angle between the two benzene rings changes in the wide range.[1–5] For example, the dihedral angles of thianthrene (X,Y=S),[1] thioxanthene (X=S, Y=CH_2),[4] and thioxanthone 10-oxide (X=SO, Y=CO)[5] are 128.1°, 135.3°, and 155.7°, respectively. On the other hand, the gas-phase electron diffraction study of thianthrene[6] has shown that this molecule vibrates with large amplitude by folding on the X–Y line, and that the minimum of the potential energy is at 128—130° of the dihedral angle.[6]



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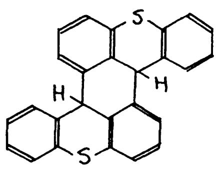

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The compound **2** was synthesized from thioxanthone (X=S,Y=CO), but it was not obtained from condensation of thioxanthene which was the half of the object compound.[7] The difference in the molecular structures between thioxanthone and thioxanthene might be one of the factors proceeding the reaction. Thus we undertook the molecular structure determination of thioxanthone by means of a gas electron-diffraction method.

Experimental

O-Mercaptobenzoic acid was allowed to react with sulfuric acid in benzene by heating on a water bath. The crude product was purified by recrystallization from acetic acid solution, and then by sublimation in vacuum.

Electron diffraction photographs were taken by the use of an r^3-sector on Kodak Electron-Image plates at camera distances of 293.70 and 143.98 mm. The sample was sublimed at 455 K by a high-temperature nozzle. The accelerating voltage was 40 kV and the wavelength was determined from the diffraction patterns of thallium(I) chloride.[8] The exposure times were about 60 and 130 s for the long and the short camera-distance photographs, respectively, with an electron-beam current of 0.7 μA. The pressure in the diffraction chamber was 6.7×10^{-4} Pa during the experiment. Four and three plates were selected for the long and the short camera-distance photographs, respectively, and their optical densities were measured at 0.4 mm intervals by the use of a digital microphotometer. The electron diffraction unit and the digital microphotometer used in the present study have been described elsewhere.[9]

Analysis and Results

The scattering intensities in the range of q=9.0—52.5 Å^{-1} were obtained from the long camera-distance

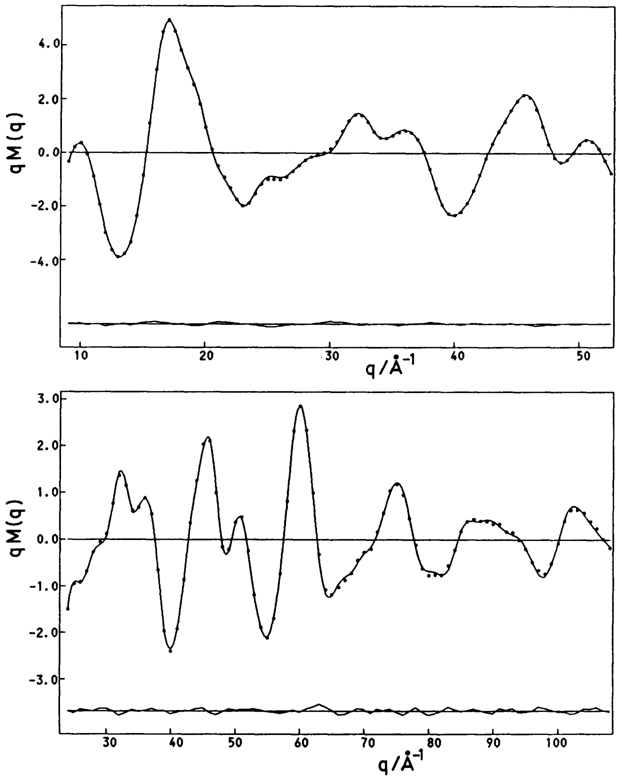

Fig. 1. Molecular intensities for thioxanthone. The upper figure shows the long camera-distance data and the lower figure the short camera-distance data. Dots represent the observed ones and solid curves the calculated ones. The residuals are shown at the lower parts of the figures.

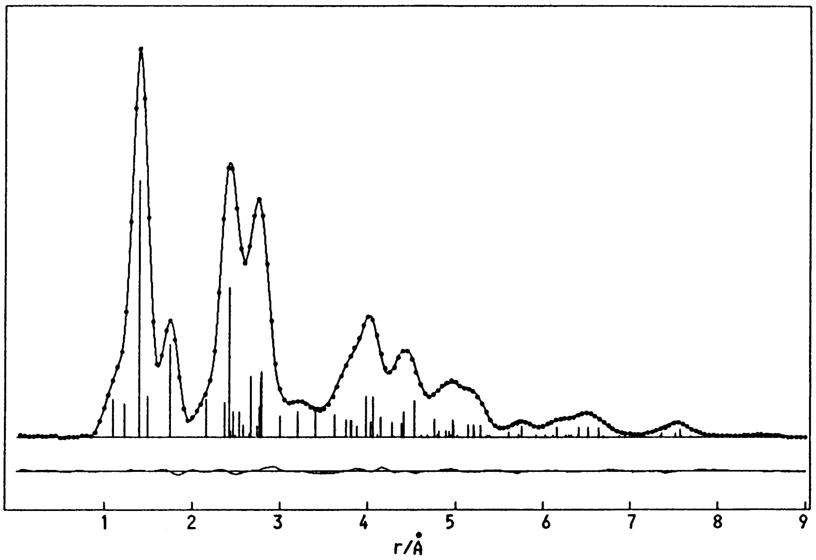

Fig. 2. Radial distribution curve for thioxanthone. Dots represent the experimental one, solid curve the theoretical one, and the difference is shown below. The vertical bars represent bond distances and the scattering powers.

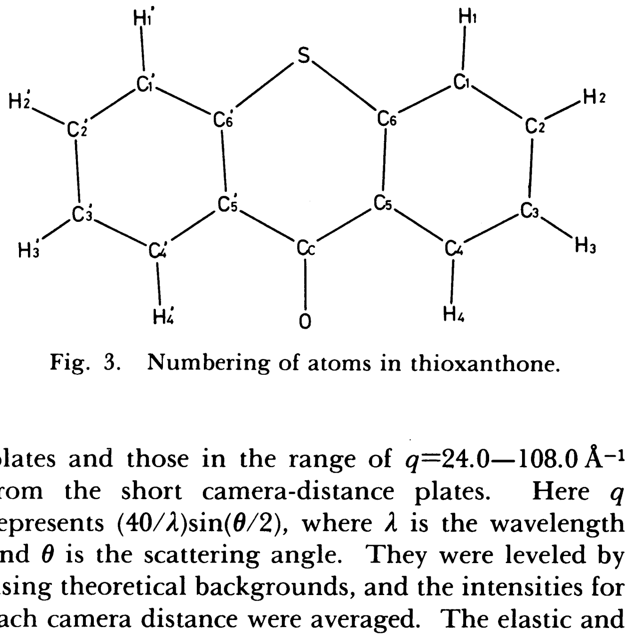

Fig. 3. Numbering of atoms in thioxanthone.

Table 1. Urey-Bradley Force Field for Thioxanthone

K(C-C)	5.46	*H*(CC(O)C)	0.15
K(C-H)	4.56	*H*(CCO)	0.40
K(C-S)	2.00	π(H)	0.30
K(C-C(O))	3.70	π(O)	0.62
K(C-O)	10.5	π(S)	0.50
Y(C-C)	0.20	π(C(O))	0.50
Y(C-S)	0.15	*F*(CC)	0.37
Y(C-C(O))	0.15	*F*(CH)	0.54
H(CCC)	0.33	*F*(CS)	0.50
H(CCH)	0.20	*F*(CC(O))	0.30
H(CCS)	0.15	*F*(CO)	0.40
H(CSC)	0.15	*F*(C(S)C)	0.20
H(CCC(O))	0.15	*F*(C(CO)C)	0.30

The potential function was defined as $V=1/2\sum K\Delta r^2 + 1/2\sum H(r\Delta\theta)^2 + 1/2\sum F\Delta q^2 + 1/2\sum Y\Delta\tau^2 + 1/2\sum \pi\Delta\sigma^2$, where the force constants of bond stretching, *K*, angle deformation, *H*, and repulsion between nonbonded atoms, *F*, are in $10^2\,\mathrm{N\,m^{-1}}$, while those of torsion, *Y*, and out-of-plane, π, are in $10^{-18}\,\mathrm{N\,m}$.

plates and those in the range of q=24.0—108.0 Å^{-1} from the short camera-distance plates. Here q represents $(40/\lambda)\sin(\theta/2)$, where λ is the wavelength and θ is the scattering angle. They were leveled by using theoretical backgrounds, and the intensities for each camera distance were averaged. The elastic and inelastic scattering factors were taken from the tables prepared by Schäfer et al.[10] and by Cromer,[11] respectively. The inelastic scattering factor for hydrogen atom was taken from the table by Tavard et al.[12] The experimental molecular intensities obtained are shown in Fig. 1. Figure 2 shows the experimental radial distribution function, which is the Fourier transform of the modified molecular intensities, $qM(q)\exp(-bq^2)$, where the damping factor b was 0.0002 in the present study. The molecular model of thioxanthone and the numbering of the atoms are shown in Fig. 3.

The molecular parameters were obtained from least-squares analysis of the molecular intensities on the basis of the following assumption: 1) The molecule has C_s symmetry. 2) The benzene ring is a regular hexagon. 3) The sulfur and carbonyl carbon atoms are on the plane of the benzene ring. 4) The oxygen atom is on the $C_5C_cC_5'$ plane. With these assumption,the geometrical papameters, r_α,[13] refined by least-squares analysis were as follow; $r(C_1-C_2)$, $r(C_1-H_1)$, $r(C_6-S)$, $r(C_5-C_c)$, $r(C_c-O)$, $\angle SC_cC_5$, $\angle C_cC_5C_6$, and θ(dihedral angle).

The vibrational mean amplitudes and the shrinkage corrections, r_a-r_α,[13] were calculated from a Urey-Bradley force field. Since the normal vibration analysis of this molecule has not been performed, the force constants were refered from thianthrene[6] and acetone,[14] as listed in Table 1. The calculated mean

Table 2. Root-Mean-Square Amplitudes and Shrinkage Corrections for Thioxanthone (in 10^{-4} Å)

Atomic pair	l	r_a-r_α	Atomic pair	l	r_a-r_α
C_1–C_2	456	103	$C_4\cdots S$	697	50
$C_1\cdots C_3$	602	123	$C_4\cdots C_c$	739	74
$C_1\cdots C_4$	676	98	$C_4\cdots O$	1112	120
C_1–H_1	768	181	$C_5\cdots C_5'$	676	20
$C_1\cdots H_2$	971	218	$C_5\cdots C_6'$	774	8
$C_1\cdots H_3$	967	231	$C_5\cdots S$	655	24
$C_1\cdots S$	734	84	$C_5\cdots C_c$	500	35
$C_1\cdots C_c$	681	41	$C_5\cdots O$	654	90
$C_1\cdots O$	817	59	$C_6\cdots C_6'$	753	17
$C_2\cdots S$	745	100	C_6–S	557	43
$C_2\cdots C_c$	750	73	$C_6\cdots C_c$	638	14
$C_2\cdots O$	1016	92	$C_6\cdots O$	710	47
$C_3\cdots S$	755	82	$S\cdots C_c$	773	2
$C_3\cdots C_c$	752	91	$S\cdots O$	860	16
$C_3\cdots O$	1137	121	C_c–O	386	94

The numbering of the atoms is shown in Fig. 3.

Table 3. Molecular Parameters Obtained from Least-Squares Analysis for Thioxanthone

	r_α	r_g	ε a)
$r(C_1$–$C_2)$/Å	1.389	1.401	0.001
$r(C_1$–$H_1)$/Å	1.077	1.099	0.007
$r(C_6$–$S)$/Å	1.745	1.751	0.002
$r(C_5$–$C_c)$/Å	1.491	1.498	0.004
$r(C_c$–$O)$/Å	1.220	1.232	0.006
$\angle SC_cC_5$/°	60.2		0.3
$\angle C_cC_5C_6$/°	123.2		0.3
θ/° b)	169.0		1.6
$\angle C_6SC_6'$/° c)	103.4		0.3
$\angle C_5C_cC_5'$/° c)	119.4		0.6

a) Limits of error (see text). b) Dihedral angle. c) Dependent parameter.

amplitudes and the shrinkage corrections of some atomic pairs which give a large contribution to the electron diffraction intensities are listed in Table 2. The mean amplitudes of $l(C_1$–$C_2)$, $l(C_1\cdots C_3)$, $l(C_1$–$H_1)$, $l(C_6$–$S)$, $l(C_5$–$C_c)$, and $l(C_c$–$O)$ were refined by the least-squares calculations, and other mean amplitudes and the shrinkage corrections were fixed to the calculated values throughout the analysis. All the asymmetry parameters, κ,[13] were ignored.

The r_g parameters were calculated from the r_a paremeters obtained in the least-squares calculations,[13] and they are listed in Table 3 with dependent parameters and their limits of error. The observed mean amplitudes are listed in Table 4. The limits of error in the distances are the square root of the sum of the squares of the random and systematic errors, and those in the angles are the random errors. The random errors were 2.6 times as large as the errors estimated by the least-squares calculations. The systematic errors were estimated from the errors in both the measurements of camera distance (0.03%) and wavelength (0.09%). The best-fit molecular intensities and the theoretical radial distribution function are shown in Figs. 1 and 2, respectively. The experimental intensities, the experimental smooth backgrounds, and the correlation matrix for the molecular parameters are deposited in Document No. 8765 at the Office of the Editor of the Bulletin of the Chemical Society of Japan. The least-squares calculations were carried out on a HITAC M-280H computer in the Computer Center of the University of Tokyo.

Table 4. Root-Mean-Square Amplitudes of Thioxanthone Obtained from Least-Squares Analysis

Atomic pair	l_{obsd}/Å a)	ε/Å b)	l_{calcd}/Å c)
C_1–C_2	0.052	0.002	0.046
$C_1\cdots C_3$	0.064	0.002	0.060
C_1–H_1	0.071	0.009	0.077
C_6–S	0.056	0.003	0.056
C_5–C_c	0.067	0.008	0.050
C_c–O	0.049	0.010	0.039

a) Values obtained by least-squares calculations. b) Limits of error (see text). c) Values calculated from the force constants in Table 1.

Discussion

The value of the C_1–C_2 distance in Table 3 represents the average of all the C–C bond distances of the benzene rings in thioxanthone because of the assumption of a regular hexagon. The lower symmetry of the benzene ring of C_{2v} with the equal C–C bond distances, where the two fold axis lies along the $C_1\cdots C_4$ bond, was assumed in the analysis, but the structure of the benzene ring converged to a regular hexagon and the other molecular parameters agreed with the values in Table 3 within the limits of error. The observed mean amplitude of the C_1–C_2 bond is a little larger than the calculated value, but we did not try the further analysis, because the force constants used to calculate the mean amplitudes were tentative ones transfered from the related molecules.

The molecular parameters of thioxanthone and related molecules are listed in Table 5. The C–C and C–H distances of the benzene ring in thioxanthone are in good agreement with those of benzene.[15] The C–O distance of the central ring is much longer than that of acetone,[16] and the mean amplitude of this bond is larger than the calculated value. These facts seem to indicate that the double bond character of carbonyl group decreases in a cyclic molecule. Infrared absorption spectra showed similarly that the wave number of the C–O stretching in thioxanthone,

Table 5. Comparison of Molecular Parameters

	Thioxanthone	Thioxanthone 10-oxide	Thioxanthene	Thianthrene	Benzene	Acetone	Dimethyl sulfide
r(C-C)/Å	1.401(1)	1.386(12)[a]	1.386(6)[a]	1.400(2)	1.399(1)		
r(C-H)/Å	1.099(7)			1.082(22)	1.101(5)		
r(C-S)/Å	1.751(2)	1.788(3)	1.77(1)	1.770(3)			1.807(2)
r(C-C$_c$)/Å	1.498(4)	1.483(5)	1.50(1)			1.520(3)	
r(C$_c$-O)/Å	1.232(6)	1.223(5)				1.213(4)	
∠CSC/°	103.4(3)	99.0(2)	99.2(3)	104.1			99.05(4)
Dihedral angle/°	169.0(16)	155.7	135.3	131.4(3)			
Reference	This work	5	4	6	15	16	17

Distance parameters of gas molecules are r_g parameters.

[a] Average value of C-C distances in the benzene rings.

1645 cm^{-1}, was much lower than that in acetone, 1738 cm^{-1}.[14)]

Gillean et al. have shown that the C-S and C-C distances in the central ring of a heterocyclic molecule are in the range of 1.77—1.78 Å and 1.50—1.53 Å, respectively, and that they are insensitive to the oxidation state of sulfur atom and substitutions on the central carbon atom.[4)] The C-S distance of gaseous thioxanthone, however, is 0.02 Å short out of the above range. The CSC angle is about 4° larger than the corresponding values of the other related molecules, though it is in agreement with that of gaseous thianthrene.[6)]

The dihedral angle between the two benzene rings in thioxanthone is notably larger than those of thianthrene[6)] and thioxanthene.[4)] The flatness of the molecular plane of thioxanthone may be due to the sp^2 hybridization of the carbonyl carbon. Gallaher and Bauer have pointed out in the electron diffraction study[6)] that thianthrene vibrates with large amplitude. However, we could not detect such a large amplitude motion in the analysis of thioxanthone. The inversion motion of thioxanthone may be also fixed by the carbonyl group of the central ring.

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