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## Crystal Structure of 3,4-Furandicarboxylic Acid<sup>1</sup>

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RECEIVED NOVEMBER 26, 1963

The crystal structure of 3,4-furandicarboxylic acid has been determined, and the three-dimensional scintillation counter data have been refined by anisotropic least-squares analysis. The furan ring is planar, with a crystallographic symmetry plane normal to the ring plane and passing through the ring oxygen atom. The carboxyl groups are slightly tilted and rotated 3.8° from the ring plane. An intramolecular hydrogen bond of length 2.555 Å. joins the two carboxyl groups. The molecules are joined into chains by an intermolecular hydrogen bond of length 2.639 Å. The hydrogens in these bonds must lie on mirror planes and centers of symmetry, respectively, or must be disposed symmetrically about these symmetry elements, either statistically or in double wells. Thermal parameters seem to eliminate statistical averaging. The abnormal isotope effect (Robertson-Ubbelohde effect) may prove useful in distinguishing between single and double well distributions.

### Introduction

The acid dissociation constants of the furandicarboxylic acids have been determined by Oae, Hamada, Otsuji, and Furukawa.<sup>3</sup> A very large difference between the values of the first and second ionization constants was found for the 2,3- and the 3,4-diacids. It seemed reasonable to conclude, as did Oae, *et al.*, that a very strong intramolecular hydrogen bond existed in 2,3- and 3,4-furandicarboxylic acid. Infrared absorption data also indicated the existence of a short intramolecular hydrogen bond. The present authors found that the 3,4-diacid was suitable for an X-ray structural study of the hydrogen bonding in these compounds.

### Collection and Treatment of X-Ray Data

Dr. Hamada kindly supplied us with crystals of the disodium salt of 3,4-furandicarboxylic acid. The acid was prepared by acidification with HCl and recrystallization from water solution. The colorless monoclinic needles were found, as the result of the structure determination, to have space group symmetry  $P2_1/m$ . The lattice constants were obtained by a least squares extrapolation treatment of data for 18 reflections in the back reflection region, using the single crystal orienter with chromium radiation. The single crystal orienter was previously calibrated with an aluminum single crystal. The lattice constants obtained at room temperature are:  $a = 6.0629 \pm 0.0006$ ,  $b = 3.6677 \pm 0.0004$ ,  $c = 14.4126 \pm 0.0014$ , and  $\gamma = 92.60 \pm 0.06$ .

The density calculated on the basis of two molecules in the unit cell is 1.57 g. cm.<sup>-3</sup>. The crystals were elongated along  $b$ , and cleaved easily along  $(\bar{1}10)$  planes.

Complete three-dimensional X-ray diffraction intensity data (up to  $\sin \theta/\lambda = 1.15$ ) were taken with molybdenum radiation from a crystal approximately 0.30 mm. long and 0.18 mm. in diameter. A General Electric XRD-5 X-ray unit equipped with a single crystal orienter and scintillation counter was used with the moving-crystal-moving-counter measurement technique ( $\theta$ ,  $2\theta$  coupling), 3.0° take-off angle, and a 2.8° diffracted beam aperture. A pulse selector admitted pulses to the scaler between 5 and 15 v., with the pulse distribution being centered in the selector window by varying the supply voltage to the scintillation counter photomultiplier. A zirconium foil was placed in the diffracted beam path. A 200-sec. scan, covering 3.33°

in  $2\theta$  was used for each reflection, followed by a repeat scan for background with an  $\omega$  offset of 1.8°; all angles were set by hand and the average rate of measurement was six reflections per hour. Two standard reflections, (010) and (006), were measured periodically; the intensity of these reflections remained constant within  $\pm 3\%$ . Single crystal orienter settings were precalculated<sup>4</sup> on the Cyclone computer. A total of 768 reflections was measured.

**Streak Correction.**—With the experimental conditions used a considerable amount of noncharacteristic radiation in the wave length range  $\lambda_k < \lambda < 2\lambda_k$  was admitted into the counter window. This "streaking" is more intense with a molybdenum target tube than with a copper target tube for the usual experimental conditions. The ratio of characteristic to noncharacteristic radiation is highest when the applied voltage is approximately four times the excitation voltage of the target used.<sup>5</sup> For copper and molybdenum targets the optimum applied voltages are 36 and 80 kv. d.c., respectively. Since our present power supplies and X-ray tubes are limited to 50 kv. pk., Mo target tubes show a considerably lower characteristic to noncharacteristic radiation ratio than Cu target tubes.

Streaking may be eliminated by use of a crystal monochromator, but only with a large loss of incident beam intensity. Also, balanced filters (Ross filters) may be used to isolate the characteristic radiation component, although much less completely than with a crystal monochromator. This method is tedious since the filters must be accurately balanced, and it is necessary to make two intensity measurements and two background measurements for each reflection.

If, however, the noncharacteristic intensity distribution of the X-ray source is measured, a streak correction may be routinely applied to the observed data to eliminate noncharacteristic radiation components.

If the observed counting rate in the neighborhood of the characteristic wave length is approximated by a Gaussian, the observed integrated intensity  $I_k$  is

$$I_k = \int_{-\infty}^{+\infty} P_k \exp[-(\ln 2)\theta_{1/2}^{-2}(\theta_k - \theta)^2] d\theta$$

$$= P_k \pi^{1/2} (\ln 2)^{-1/2} \theta_{1/2}$$

where  $P_k$  is the peak counting rate,  $\theta_k$  is the characteristic Bragg angle, and  $\theta_{1/2}$  is the half-width at half-height

(1) Contribution No. 1407. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) Deceased, October 9, 1963.

(3) S. Oae, M. Hamada, Y. Otsuji, and N. Furukawa, *Ann. Rept. Radiation Center Osaka Prefect.*, **2**, 106 (1961).

(4) D. E. Williams, "Single Crystal Orienter Program SCO-5," unpublished research.

(5) G. D. Rieck, "International Tables for X-Ray Crystallography," Vol. III, K. Lonsdale, Ed., Kynoch Press, Birmingham, 1962, p. 59.

of the Gaussian. This approximation assumes that the scan length is long enough that the value of the integrand is negligible outside the scan range. The wave length range,  $\Delta\lambda_k$ , is associated with the half-width constant,  $\theta_{1/2}$ . The observed integrated streak intensity,  $I_s$ , may be approximated by the integral

$$I_s = \int_{\theta - (\Delta\theta_s/2)}^{\theta + (\Delta\theta_s/2)} P_s d\theta = \bar{P}_s \Delta\theta_s$$

where  $P_s$  is the streak counting rate and  $\Delta\theta_s$  is the scan length. Associated with the scan length is the wave length increment,  $\Delta\lambda_s$ .

For the reference reflection,  $r$ , the relation between the wave length increment,  $\Delta\lambda_r$ , and the fixed scan length,  $\Delta\theta_s$ , is given by the formula

$$\Delta\lambda_r = 2d_r \cos \theta_r \sin (\Delta\theta_s)$$

where  $d_r$  is the interplanar distance.

The quantity  $W'(\lambda)$  may conveniently be defined as the relative experimental wave length distribution, corrected for the Lorenz factor,  $L$ , the polarization factor,  $p$ , and the wave length increments,  $\Delta\lambda_k$  and  $\Delta\lambda_r$

$$W'(\lambda) = \frac{I_s L_k p_k \Delta\lambda_k}{I_k L_s p_s \Delta\lambda_r} = \frac{I_s L_k p_k \Delta\lambda_k}{I_k L_s p_s 2d_r \cos \theta_r \sin (\Delta\theta_s)}$$

In terms of  $W'(\lambda)$ , the streak contribution to reflection  $n$  caused by a streak from reflection  $m$  is given by

$$I_s^m = \frac{I_k L_n p_n 2d_m \cos \theta_n \sin (\Delta\theta_s) W'(\lambda)}{L_m p_m \Delta\lambda_k}$$

where  $W'$  is evaluated at  $\lambda_m/\lambda_k = d_m/d_n$ . Canceling common factors, the following equation is obtained

$$I_s^m = \left[ \frac{I_k L_n p_n d_m \cos \theta_n}{L_m p_m} \right] \left[ \frac{I_s L_k p_k}{I_k L_s p_s d_r \cos \theta_r} \right]$$

The quantity in the second brackets,  $W(\lambda)$ , may conveniently be tabulated *vs.*  $\lambda/\lambda_k$  from experimental data.

The process of correcting for streaking consists of subtracting all significant streaking contributions from the characteristic reflection intensity

$$I_k^n \text{ (streak corrected)} = I_k^n \text{ (uncorrected)} - \sum_m I_s^m$$

The reflections to be summed are along a line through the characteristic reflection point and the origin of the reciprocal lattice.

In the fixed-crystal, fixed-counter, divergent source technique, the fixed scan  $\Delta\theta_s$  is replaced by a divergent source of fixed angular width  $\Delta\theta_f$ . If  $\Delta\theta_f$  is sufficiently broad so that the count rate is negligible outside of the angular interval, the situation is completely equivalent to the moving-crystal, moving-counter method, and the same formulas are applicable.

A streak correction for the wave length range  $\lambda_k < \lambda_s \leq 2\lambda_k$  was applied to the 3,4-furandicarboxylic acid intensities, in addition to the usual Lorenz and polarization corrections. No absorption or extinction corrections were made; an exception was the  $(\bar{1}10)$  reflection, which was not included in the least squares refinement because its intensity appeared to be reduced by extinction. A counter nonlinearity correction was applied to all crude counting rates.

The streak correction is most important along densely packed radial reciprocal lattice lines; Table I illustrates

the importance of this correction for the densely packed  $(00l)$  reflections. Of the total of 768 reflections, 108 had a significant streak correction.

TABLE I  
STREAK CORRECTION DATA

<i>hkl</i>	Counts (uncor.)	Streak counts	$F_o$ (uncor.)	$F_o$ (cor.)	$F_e$ (final model)
002	1,013,560	0	382	382	-355
004	71,500	8,354	143	134	-117
006	133,300	6,884	240	234	228
008	50,240	18,654	172	136	-130
0, 0, 10	47,580	8,233	190	173	-171
0, 0, 12	8,420	6,915	89	37	-16
0, 0, 14	4,460	2,966	72	41	-35
0, 0, 16	1,620	1,126	47	26	21
0, 0, 18	440	453	26	0	7
0, 0, 20	420	141	28	23	20

**Treatment of Errors and "Unobserved" Reflections.**—The estimated error in each intensity measurement was calculated by the formula

$$(\Delta I)^2 = C_T + C_B + (K_T C_T)^2 + (K_B C_B)^2 + (K_S C_S)^2$$

where  $C_T$ ,  $C_B$ , and  $C_S$  are the total, background, and streak counts, respectively. In addition to the usual statistical errors, this formula assumes relative errors of  $K_T$ ,  $K_B$ , and  $K_S$  in the total, background, and streak counts, respectively.  $K_T$  and  $K_B$  were assigned values of 0.02 corresponding to a 2% nonstatistical fluctuation in the peak and background counts.  $K_S$  was assigned a value of 0.05 corresponding to a 5% error in the streak correction.

When using the counter technique it is unnecessary to distinguish between observed and "unobserved" reflections. However, the usual infinitesimal formula relating the error in the intensity to the error in the structure factor is undefined when the intensity is measured as zero. By using the finite difference method, the following formula may be derived to relate these quantities

$$\Delta F = (Lp)^{-1/2} [-I^{1/2} + (I + \Delta I)^{1/2}]$$

This formula was used for 3,4-furandicarboxylic acid, and all reflections, correspondingly weighted, were included as observed in the refinement of this structure.

### Structure Determination

The  $(\bar{1}10)$  reflection was found to be very intense, and this fact, along with the easy cleavage along  $(\bar{1}10)$ , indicated that the planar 3,4-furandicarboxylic acid molecules were approximately parallel to this plane. In this arrangement, the mirror plane at  $z = 1/4$  of the space group  $P2_1/m$  must coincide with the mirror plane of the molecule normal to the plane of the molecule. The only remaining degree of freedom is, then, along the  $(\bar{1}10)$  plane. This parameter was found by examining possible intermolecular hydrogen-bonding configurations between adjacent molecules in the  $z$  direction.

Two models were hypothesized, one with a *trans* intermolecular hydrogen bond and a second with a *cis* bond, using conventional bond distances and angles. The second model proved correct as indicated by the convergence of the model when subjected to a full matrix least squares treatment. The program of Busing and Levy<sup>6</sup> was used for the refinement. The scattering

(6) W. Busing and H. Levy, "A Crystallographic Least Squares Refinement Program for the IBM 704," ORNL 59-4-37, 1960.

TABLE II  
FINAL VALUES OF THE PARAMETERS AND THEIR STANDARD DEVIATIONS  
The form of the temperature factor is  $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$

Atom	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
O <sub>1</sub>	0.6218	0.4713	0.2500	0.0197	0.0968	0.0057	-0.0153	0.0000	0.0000
$\delta$	.0004	.0007	.0000	.0008	.0028	.0002	.0012	.0000	.0000
C <sub>2</sub>	.5000	.3743	.1743	.0221	.0808	.0050	-.0084	.0009	.0015
$\delta$	.0004	.0008	.0002	.0008	.0027	.0002	.0012	.0003	.0005
C <sub>3</sub>	.3037	.2188	.1996	.0186	.0595	.0038	-.0034	.0004	.0006
$\delta$	.0004	.0007	.0002	.0007	.0020	.0001	.0009	.0002	.0004
C <sub>4</sub>	.1342	.0829	.1335	.0234	.0726	.0044	-.0044	-.0001	-.0017
$\delta$	.0004	.0007	.0002	.0008	.0024	.0001	.0011	.0003	.0005
O <sub>5</sub>	-.0412	-.0793	.1617	.0216	.1065	.0046	-.0185	-.0002	-.0015
$\delta$	.0003	.0006	.0001	.0005	.0020	.0001	.0008	.0002	.0004
O <sub>6</sub>	.1709	.1318	.0489	.0324	.1414	.0036	-.0256	.0001	.0008
$\delta$	.0003	.0006	.0001	.0007	.0025	.0001	.0010	.0002	.0004
H <sub>7</sub>	.566	.439	.115	.019	.094	.004	-.009	.004	.009
$\delta$	.005	.009	.002	.011	.035	.000	.017	.004	.007
H <sub>8</sub>	-.046	-.082	.250	.034	.092	.024	.002	.000	.000
$\delta$	.010	.017	.000	.000	.000	.000	.000	.000	.000
H <sub>9</sub>	.000	.000	.000	.131	.150	.014	.078	.028	.021
$\delta$	.000	.000	.000	.000	.000	.000	.000	.000	.000

factors of Berghuis, *et al.*,<sup>7</sup> were used for the carbon and oxygen atoms, and those of James and Brindley<sup>8</sup> for the hydrogen atoms.

5%. However, the anisotropic thermal parameters of the hydrogen atoms were unsatisfactory.

Several attempts were made to refine a model with statistical hydrogen locations in the hydrogen bonds. It was concluded that the data were insufficient to distinguish between statistical hydrogen positions and symmetric hydrogen positions with a large thermal anisotropy.

For the final model all positional parameters were allowed to vary, along with anisotropic thermal parameters of the heavy atoms. It was necessary to hold the  $\beta_{33}$  thermal parameter of the furan ring hydrogen constant because of the tendency of this parameter to decrease to a negative value. The parameter  $\beta_{33}$  of this atom would be expected to be small since it describes the thermal amplitude nearly parallel to the furan ring C-H bond. The other five anisotropic parameters for this hydrogen were varied, however. The hydrogen-bonded hydrogens were placed symmetrically between the oxygen atoms. A large thermal anisotropy of these hydrogens was assumed in the direction of the hydrogen bonds, and all anisotropic thermal parameters for these hydrogen-bonded hydrogens were held constant.

The final discrepancy index was 4.7%. The quantity  $[\sum w(F_o - F_c)^2 / (m - n)]^{1/2}$  was 1.19, indicating a reasonable assignment of weighting factors. Table II lists the final parameters that were obtained. Table III lists the observed and calculated structure factors.

### Discussion

Table IV and Fig. 1 show the intramolecular distances and angles and their estimated standard deviations. In calculating the estimated standard deviations the complete variance-covariance matrix was used; these calculations were made with the program of Busing and Levy.<sup>9</sup> The third column of the table gives distances corrected for rigid body libration as explained below; this correction is negligible for the angles. For comparison, Table IV also shows the distances and angles found by Bak<sup>10</sup> in his careful microwave structure determination of furan itself.

(9) W. Busing and H. Levy, "A Crystallographic Function and Error Code for the IBM 704," ORNL 59-12-39, 1959.

(10) B. Bak, D. Christensen, W. Dixon, L. Hansen-Nygaard, J. Andersen, and M. Schottländer, *J. Mol. Spectry.*, **9**, 124 (1962).

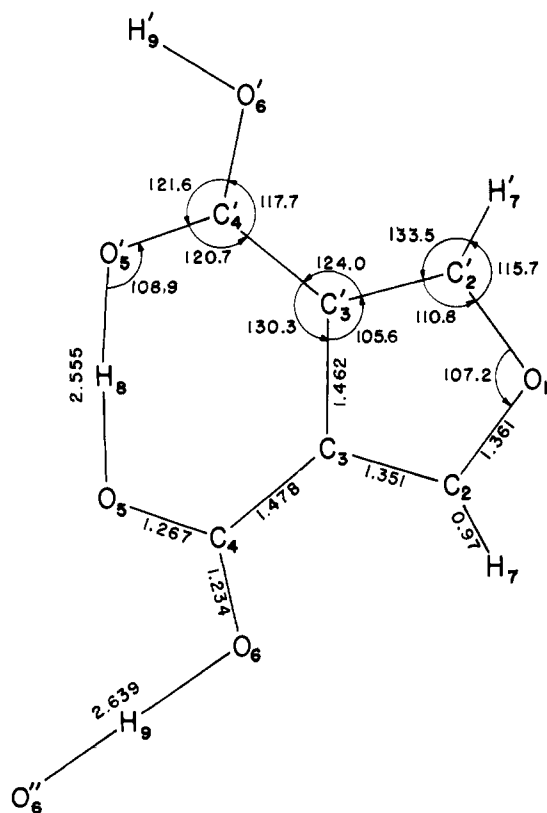


Fig. 1.—Intramolecular distances and angles, corrected for rigid body libration.

Refinement using isotropic individual atomic thermal parameters yielded a discrepancy index of 13%. When allowance for anisotropic thermal vibration was made, the discrepancy index decreased to 7%. At this point all hydrogen atoms were included in the model, and both the thermal and positional parameters of the hydrogens were varied. The discrepancy index dropped to

(7) J. Berghuis, I. Haanappel, M. Potters, B. Loopstra, C. MacGillavry, and A. Veenendaal, *Acta Cryst.*, **8**, 478 (1955).

(8) R. James and G. Brindley, *Phil. Mag.*, [7] **12**, 81 (1931).



TABLE IV  
 INTRAMOLECULAR DISTANCES AND ANGLES AND THEIR ESTIMATED STANDARD DEVIATIONS

Atoms	Distance (uncor.), Å.	Distance (cor.), Å.	Furan, <sup>10</sup> Å.	Atoms	Angle	Furan <sup>10</sup>
O <sub>1</sub> -C <sub>2</sub>	1.356 ± 0.003	1.361	1.362 ± 0.001	C <sub>2</sub> -O <sub>1</sub> -C <sub>2</sub> '	107.2 ± 0.3°	106.6 ± 0.1°
C <sub>2</sub> -C <sub>3</sub>	1.346 ± .003	1.351	1.361 ± .001	O <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	110.8 ± 0.2	110.7 ± .1
C <sub>3</sub> -C <sub>3</sub> '	1.454 ± .005	1.462	1.431 ± .002	O <sub>1</sub> -C <sub>2</sub> -H <sub>7</sub>	115.7 ± 1.8	115.9 ± .1
C <sub>3</sub> -C <sub>4</sub>	1.472 ± .003	1.478		C <sub>3</sub> -C <sub>2</sub> -H <sub>7</sub>	133.6 ± 1.8	133.4 ± .1
C <sub>4</sub> -O <sub>5</sub>	1.262 ± .003	1.267		C <sub>2</sub> -C <sub>3</sub> -C <sub>3</sub> '	105.7 ± 0.2	106.1 ± .1
C <sub>4</sub> -O <sub>6</sub>	1.251 ± .003	1.254		C <sub>2</sub> -C <sub>3</sub> -C <sub>4</sub>	124.0 ± .2	125.9 ± .1 <sup>a</sup>
O <sub>5</sub> -O <sub>5</sub> '	2.544 ± .004	2.555		C <sub>4</sub> -C <sub>3</sub> -C <sub>3</sub> '	130.3 ± .2	128.0 ± .1 <sup>a</sup>
O <sub>6</sub> -O <sub>6</sub> '	2.652 ± .004	2.639		C <sub>3</sub> -C <sub>4</sub> -O <sub>5</sub>	120.7 ± .2	
C <sub>2</sub> -H <sub>7</sub>	0.97 ± .03		1.075 ± 0.002	C <sub>3</sub> -C <sub>4</sub> -O <sub>6</sub>	117.7 ± .2	
				O <sub>5</sub> -C <sub>4</sub> -O <sub>6</sub>	121.6 ± .2	
				C <sub>4</sub> -O <sub>5</sub> -O <sub>5</sub> '	108.9 ± .2	
				C <sub>4</sub> -O <sub>5</sub> -H <sub>8</sub>	110.1 ± 2.6	
				C <sub>4</sub> -O <sub>5</sub> -H <sub>9</sub>	109.5 ± 0.2	

<sup>a</sup> Angle to hydrogen atom.

type.<sup>14</sup> The single bond in 1,3-butadiene is reported as  $1.483 \pm 0.010$  by electron diffraction,<sup>15</sup> and as  $1.476 \pm 0.010$  Å. by infrared-Raman spectroscopy.<sup>16</sup> A microwave investigation of acrolein yielded  $1.472$  Å. as the trigonal-trigonal C-C distance.<sup>17</sup> On the other hand, a

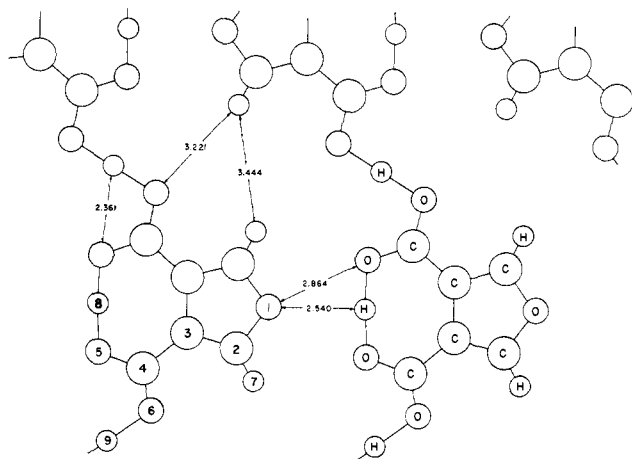


Fig. 2.—The structure projected onto the ring least squares plane.

very careful investigation of 1,3,5,7-cyclooctatetraene by electron diffraction yielded  $1.462 \pm 0.001$  for the single bond length.<sup>18</sup> If the cyclooctatetraene value is rejected as abnormal, the ring-carboxyl distance in this structure is very close to the average ( $1.477$  Å.) of the above three quoted distances for butadiene and acrolein.

The two carboxyl C-O distances of  $1.267$  and  $1.254$  Å. differ by only  $0.013$  Å., but this difference should be significant if the estimated standard deviations of  $0.003$  Å. in the individual distances are correct. The longer C-O distance corresponds to the shorter hydrogen bond and *vice versa*.

The intramolecular hydrogen bond is of length  $2.555$  Å. The small observed departure from collinearity is not significant. The C-O-H bond angle is very nearly tetrahedral. The molecules are joined into chains in the *c*-lattice direction by intermolecular hydrogen

(14) See, for example, "An Epistalogue on Carbon Bonds," *Tetrahedron*, **17**, No. 3/4 (1962).

(15) A. Almennigen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958).

(16) D. Marais, N. Sheppard, and B. Stoicheff, *Tetrahedron*, **17**, 163 (1962).

(17) C. Costain and E. Chernick, quoted by B. Stoicheff, *ibid.*, **17**, 144 (1962).

(18) O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, **27**, 1311 (1957).

bonds of length  $2.639$  Å. (Fig. 2). These bonds are collinear by symmetry, and again the observed C-O-H bond angle is nearly tetrahedral. Both hydrogens in the hydrogen bonds are in crystallographic special positions, the intramolecular bond being across a mirror, and the intermolecular bond being across a center of symmetry.

The furan ring is accurately planar; the equation of the least squares plane and atomic distances from the plane are given in Table V. The carboxyl oxygen atoms are significantly out of the ring plane; the twist angle of the carboxyl group relative to the ring plane is  $3.8^\circ$ . The twist of the carboxyl group, and also the slight displacement of the carboxyl carbon, is such as to move O<sub>5</sub>, the intramolecular hydrogen bonded oxygen, closer to the furan ring oxygen in the diagonally adjacent unit cell (see closest intermolecular approaches discussed below).

TABLE V  
 DISTANCES FROM THE RING LEAST SQUARES PLANE IN Å.  
 (The equation of the plane is  $-0.4402X + 0.8980Y + 0.0749Z = 0$  with cartesian axes *X* and *Z* parallel to unit cell axes *a* and *c*.)

Atom	Distance	Atom	Distance
O <sub>1</sub>	0.0005	O <sub>6</sub>	0.062
C <sub>2</sub>	- .0004	H <sub>7</sub>	.04
C <sub>3</sub>	.0002	H <sub>8</sub>	-.08
C <sub>4</sub>	-.004	H <sub>9</sub>	.08
O <sub>5</sub>	-.082	O <sub>1</sub> <sup>a</sup>	-.692

<sup>a</sup> Furan oxygen in diagonally adjacent unit cell; this is the stepping distance.

Table VI lists the intermolecular distances less than  $3.5$  Å., uncorrected for rigid body libration. The limitingly short O-H nonbonded distance of  $2.361$  Å. between atom 51000 and atom 91000 appears important in determining the *c*-lattice constant (see Table VI for explanation of atom code). There are also very close nonbonded approaches between atom 11000 (the furan ring oxygen) and atoms 51110 and 81110 of the intramolecular hydrogen-bonding system in the diagonally adjacent unit cell. On the other hand, the distances between atoms 61000 and 73110, and 71000 and 73110, are larger than expected, resulting in a small hole in the structure. The molecules are not quite in the ( $\bar{1}10$ ) crystallographic plane. This leads to stepping distance of  $0.692$  Å. between molecules, as may be seen from Table V. The perpendicular distance between furan ring planes is  $3.371$  Å.

TABLE VI

NEAREST NONBONDED NEIGHBOR DISTANCES LESS THAN 3.5 Å  
(The atoms are identified by a five digit code; the first digit is the atom number (see Fig. 1 and 2), the second the symmetry transformation applied, and the third, fourth, and fifth the number of cell translations  $a$ ,  $b$ , and  $c$ , respectively. The numbers of the symmetry transformations are (1)  $x, y, z$ ; (2)  $x, y, 1/2 - z$ ; (3)  $-x, -y, -z$ ; (4)  $-x, -y, 1/2 + z$ .)

Atom 1	Atom 2	Dis- tance	Atom 1	Atom 2	Dis- tance	Atom 1	Atom 2	Dis- tance
11000	31000	2.224	31000	42000	2.655	51000	42000	3.184
	71000	1.978		52000	3.059		63000	3.140
	51100	3.201		72000	3.195			
	81100	2.924		51010	3.433	61000	71000	2.769
	31010	3.499		81010	3.477		81000	3.263
	51110	2.864					43000	3.289
	81110	2.540	41000	71000	2.885		53000	3.140
				81000	2.077		91010	3.465
21000	41000	2.489		91000	2.105		73110	3.221
	61000	2.807		32000	2.655			
	22000	2.181		42000	3.359	71000	22000	3.070
	32000	2.232		52000	3.184		32000	3.195
	72000	3.070		63000	3.289		51100	3.186
	51100	3.311		51010	3.322		51110	2.978
	81100	3.463					81110	3.470
	31010	3.387	51000	11 $\bar{1}\bar{0}$	2.864		63110	3.221
	51110	3.359		21 $\bar{1}\bar{0}$	3.359		73110	3.444
				71 $\bar{1}\bar{0}$	2.978			
31000	110 $\bar{1}\bar{0}$	3.499		310 $\bar{1}\bar{0}$	3.433	81000	11 $\bar{1}\bar{0}$	2.540
	210 $\bar{1}\bar{0}$	3.387		410 $\bar{1}\bar{0}$	3.322		71 $\bar{1}\bar{0}$	3.470
	51000	2.379		11 $\bar{1}\bar{0}$	3.201		310 $\bar{1}\bar{0}$	3.477
	61000	2.333		21 $\bar{1}\bar{0}$	3.311		11 $\bar{1}\bar{0}$	2.924
	71000	2.133		71 $\bar{1}\bar{0}$	3.186		21 $\bar{1}\bar{0}$	3.463
	81000	2.453		61000	2.193			
	91000	3.489		91000	2.361	91000	610 $\bar{1}\bar{0}$	3.465
	22000	2.232		32000	3.059		63010	3.465

TABLE VII

ANGLE  $\theta(I)$  (DEGREES) BETWEEN PRINCIPAL THERMAL AXES  $R$  AND AXES  $I$  OF A CARTESIAN COORDINATE SYSTEM DEFINED BY THE LEAST SQUARES RING PLANE

(The  $X'$ -axis is in the direction parallel to the  $XY$  plane defined by the least squares plane; the  $Y'$ -axis is perpendicular to the molecular plane.)

Atom	$R$	R.m.s.			
		amplitude (Å)	$\theta(X')$	$\theta(Y')$	$\theta(Z)$
$O_1$	1	$0.166 \pm 0.004$	$178 \pm 1$	$88 \pm 1$	$90 \pm 0$
	2	$.247 \pm .004$	$90 \pm 0$	$90 \pm 0$	$180 \pm 0$
	3	$.276 \pm .004$	$88 \pm 1$	$2 \pm 1$	$90 \pm 0$
$C_2$	1	$.183 \pm .004$	$164 \pm 4$	$85 \pm 3$	$150 \pm 4$
	2	$.232 \pm .004$	$74 \pm 4$	$81 \pm 10$	$161 \pm 6$
	3	$.249 \pm .004$	$87 \pm 4$	$11 \pm 9$	$80 \pm 10$
$C_3$	1	$.176 \pm .003$	$164 \pm 6$	$84 \pm 4$	$104 \pm 6$
	2	$.201 \pm .003$	$75 \pm 6$	$86 \pm 18$	$165 \pm 8$
	3	$.210 \pm .004$	$85 \pm 6$	$7 \pm 10$	$85 \pm 17$
$C_4$	1	$.195 \pm .004$	$156 \pm 9$	$77 \pm 5$	$70 \pm 8$
	2	$.213 \pm .004$	$113 \pm 9$	$108 \pm 8$	$150 \pm 8$
	3	$.236 \pm .004$	$95 \pm 5$	$158 \pm 5$	$69 \pm 7$
$O_5$	1	$.169 \pm .003$	$171 \pm 2$	$87 \pm 1$	$82 \pm 2$
	2	$.220 \pm .003$	$98 \pm 2$	$94 \pm 2$	$171 \pm 2$
	3	$.293 \pm .003$	$87 \pm 1$	$5 \pm 1$	$95 \pm 2$
$O_6$	1	$.193 \pm .003$	$75 \pm 9$	$93 \pm 1$	$16 \pm 9$
	2	$.207 \pm .003$	$16 \pm 8$	$95 \pm 1$	$106 \pm 9$
	3	$.341 \pm .003$	$84 \pm 1$	$6 \pm 1$	$89 \pm 1$
$H_7$	1	$.10 \pm .09$	$43 \pm 16$	$97 \pm 19$	$48 \pm 13$
	2	$.23 \pm .05$	$53 \pm 19$	$55 \pm 36$	$124 \pm 32$
	3	$.28 \pm .05$	$108 \pm 29$	$36 \pm 36$	$60 \pm 23$
$H_8$	1	$.25 \pm .00$	$0 \pm 0$	$90 \pm 0$	$90 \pm 0$
	2	$.25 \pm .00$	$90 \pm 0$	$0 \pm 0$	$90 \pm 0$
	3	$.50 \pm .00$	$90 \pm 0$	$90 \pm 0$	$0 \pm 0$
$H_9$	1	$.25 \pm .00$	$122 \pm 0$	$90 \pm 0$	$32 \pm 0$
	2	$.25 \pm .00$	$90 \pm 0$	$0 \pm 0$	$90 \pm 0$
	3	$.60 \pm .00$	$32 \pm 0$	$90 \pm 0$	$52 \pm 0$

### Analysis of Thermal Motion

The orientation and magnitudes of the principal axes of thermal vibration for the individual atoms are given

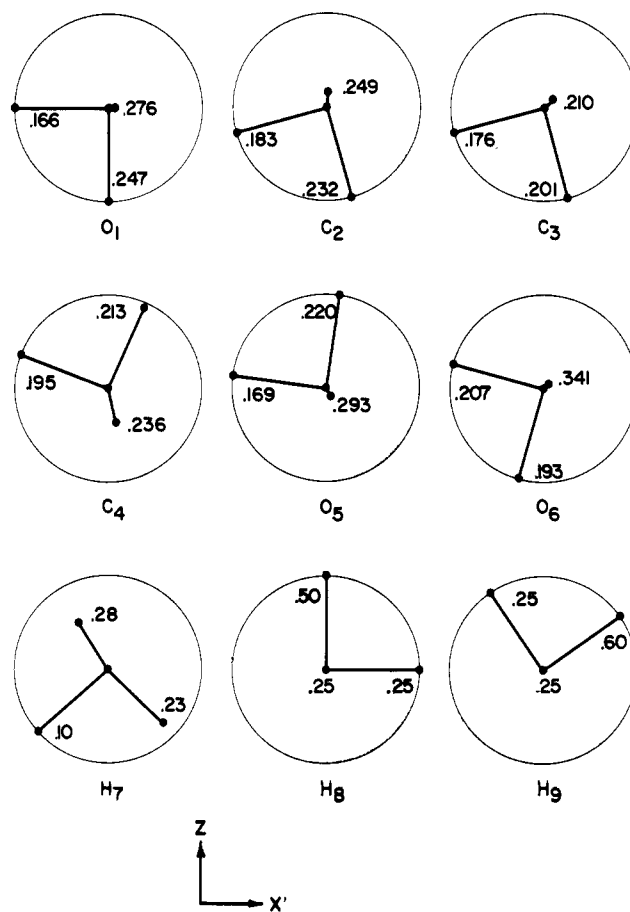


Fig. 3.—Thermal stereograms for the individual atoms. The plane of the paper is the least squares ring plane in the same orientation as Fig. 1 and 2. The directions of the principal axes of the thermaloids are shown stereographically. The root mean square amplitude is shown for each axis in Å.

in Table VII and are shown stereographically in Fig. 3. The surface described by the r.m.s. vector is not an ellipsoid, but is a surface of the fourth order.<sup>19</sup> To avoid confusion, it is suggested that this surface be referred to as a "thermaloid."

The thermal vibrations of the individual atoms are generally larger normal to the molecular plane and are generally near a minimum in the direction of a covalent bond. The thermaloids for the two hydrogen-bonded oxygen atoms, in particular, show that the observed thermal motion in the direction of the C—O bonds is small. This fact seems to rule out a statistical combination of C—O and C=O in the carboxyl groups (see additional discussion below). The crystal structures of bis(*m*-bromobenzoyl)methane<sup>20</sup> and bis(*m*-chlorobenzoyl)methane,<sup>21</sup> which have hydrogen-bonded enolic rings, have similarly small amplitudes of vibration in the direction of their C—O bonds and are also believed to be nonstatistical structures.

Because of the strong intramolecular hydrogen bond, it would be expected that the entire molecule could reasonably be approximated as a rigid body, and the individual atomic vibrations could be expressed as rigid body translations and librations by the method of Cruickshank.<sup>22</sup> Such an analysis was carried out,

(19) See, for example, J. Waser, *Acta Cryst.*, **8**, 731 (1955).

(20) D. Williams, W. Dumke, and R. Rundle, *ibid.*, **15**, 627 (1962).

(21) G. Engebretson and R. Rundle, *J. Am. Chem. Soc.*, **86**, 574 (1964).

(22) D. Cruickshank, *Acta Cryst.*, **9**, 754 (1956).

using the program UCLATO1.<sup>23</sup> The analysis was quite successful, with over 90% of the magnitudes, on the average, of the anisotropic thermal parameters  $\beta_{ij}$  being expressible as rigid body translation and libration. Table VIII gives the results of the rigid body analysis.

TABLE VIII  
RESULTS OF RIGID BODY THERMAL ANALYSIS

The translational tensor  $T$  and its estimated standard deviation

$$\begin{pmatrix} 0.0316 & -0.0025 & 0.0000 \\ & 0.0308 & .0000 \\ & & .0422 \end{pmatrix} \begin{pmatrix} 0.0014 & 0.0016 & 0.0000 \\ & 0.0021 & .0000 \\ & & .0012 \end{pmatrix}$$

Principal axes of  $T$  (Å.) and their direction cosines relative to the cartesian coordinate system defined in Table V

0.205	0.000	0.000	1.000
.184	.758	-.652	0.000
.170	.652	.758	0.000

The librational tensor  $\omega$  and its estimated standard deviation (sq. radians)

$$\begin{pmatrix} 0.0076 & 0.0031 & 0.0000 \\ & 0.0038 & .0000 \\ & & .0079 \end{pmatrix} \begin{pmatrix} 0.0004 & 0.0003 & 0.0000 \\ & 0.0003 & .0000 \\ & & .0007 \end{pmatrix}$$

Principal axes of  $\omega$  and their direction cosines (degrees)

5.5	-0.872	-0.489	0.000
5.1	.000	.000	1.000
2.6	-.489	.872	0.000

The rigid body translations are not markedly anisotropic. The largest amplitude, 0.205 Å., is in the direction of the hydrogen-bonded chain. The next largest amplitude, 0.184 Å., is very roughly perpendicular to the molecular plane. The smallest amplitude, 0.170 Å., is roughly in the molecular plane and perpendicular to the hydrogen-bonded chain.

The smallest rigid body librational axis, 2.6°, is very nearly perpendicular to the molecular plane. The other two librational axes, of amplitudes 5.1 and 5.5°, are very nearly in the molecular plane and parallel to the hydrogen-bonded chain, respectively. The smaller

(23) P. Gantzel, C. Coulter, and K. Trueblood, IBM 709 or 7090 Program UCLATO1, private communication.

libration around the axis perpendicular to the molecular plane is consistent with the tight packing along the hydrogen-bonded chains discussed under closest intermolecular approaches above.

The rigid body libration causes a shift in the apparent atomic centers toward the center of rotation (here assumed to be the center of mass of the molecule with all atoms equally weighted). Corrected atomic positions were obtained by the method of Cruickshank,<sup>24</sup> and all intramolecular distances and angles were recalculated (see Table IV). The magnitude of the librational correction for the intramolecular distances varied from 0.003 to 0.013 Å.

## Discussion

Both hydrogen bonds in this structure are at critical distances where it cannot be said with certainty that the hydrogens should be centered in a symmetrical single potential well, or distributed over a double potential well,<sup>25</sup> and, as has been noted,<sup>20,21</sup> this question cannot be settled using ordinary methods of X-ray diffraction, and probably not by neutron diffraction.<sup>26</sup>

One of the significant features of this structure determination is that it demonstrates that with careful (but not excessively time-consuming) attention to gathering and treatment of the X-ray data, and sufficient computer capacity, structures are obtainable where bond distances are reliable to about 0.01 Å. (The difficulties in attaining such accuracies have been pointed out by Cruickshank.<sup>27</sup>) This makes possible the discrimination between single and double potential wells for hydrogen bonds by the presence or absence of the abnormal isotope effect<sup>28</sup> as suggested by Rundle.<sup>29</sup>

**Acknowledgments.**—The authors are indebted to Prof. Shigeru Oae, who correctly prophesied that this compound would have a strong intramolecular hydrogen bond and led us to undertake the problem.

(24) D. Cruickshank, *Acta Cryst.*, **14**, 896 (1961).

(25) R. Blinc, D. Hadzi, and A. Novak, *Z. Elektrochem.*, **64**, 567 (1960).

(26) S. Peterson and H. Levy, *J. Chem. Phys.*, **29**, 948 (1958).

(27) D. Cruickshank, *Acta Cryst.*, **13**, 774 (1960).

(28) J. Robertson and A. Ubbelohde, *Nature*, **139**, 504 (1937).

(29) R. Rundle, paper to be published in *J. Phys. Radium* as part of the International Symposium on Neutron Diffraction, Grenoble, 1963.

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## The Anodic Oxidation of Triphenylmethane Dyes

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RECEIVED JULY 22, 1963

The anodic oxidation pathways of several typical triphenylmethane dyes have been examined in acidic buffers. The oxidation of crystal violet and malachite green leads to the formation of the oxidized form of N,N,N',N'-tetramethylbenzidine. This was shown to be an unusual reaction in which the central carbon residue is ejected followed by intracoupling to give the benzidine derivative. The role of hydrated forms of the dyes in these reactions was studied.

A previous communication reported the unusual electrochemical reaction of crystal violet and related triphenylmethane dyes which yield the diquinoid of N,N,N',N'-tetramethylbenzidine (TMBOx) upon oxidation in acidic, aqueous buffers.<sup>1</sup> Previous workers have established that the chemical oxidation of triphenylmethane dyes of this type lead to TMBOx.<sup>2-4</sup>

(1) Z. Galus and R. N. Adams, *J. Am. Chem. Soc.*, **84**, 3207 (1962).

The surprising points about the electrochemical oxidation are that the anodic reaction apparently proceeds *via* ejection of an integral unit of the central carbon attached to a phenyl group. Also, apparently only the hydrated form of the dye yields TMBOx.

(2) J. Knop, *Z. anal. Chem.*, **85**, 253 (1931).

(3) F. Kehrmann, G. Roy, and M. Ramm, *Helv. Chim. Acta*, **5**, 153 (1922).

(4) V. Hanousek and M. Matrka, *Collection Czech. Chem. Commun.*, **24**, 16 (1959).