ACTA CHEMICA SCANDINAVICA 19 (1965) 217–222

The Crystal Structure of 2,6-Dimethyl-γ-Pyrone (2,6-Dimethyl-4H-pyran-4-one) Hydrobromide Monohydrate

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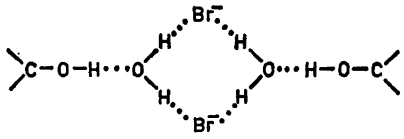
Crystals of 2,6-dimethyl-γ-pyrone hydrobromide monohydrate (DMγP·HBr·H_2O) are triclinic with the cell dimensions $a = 7.00$ Å; $b = 8.33$ Å; $c = 9.47$ Å (± 0.03 Å); $\alpha = 109.9°$; $\beta = 92.9°$; $\gamma = 106.0°$ (± 0.5°). The space group is $P\bar{1}$ and $Z = 2$. The Br, O, and C atoms were located by use of two-dimensional Patterson syntheses. The structure was refined by two-dimensional Fourier and least-squares techniques. The structure consists of centrosymmetric groups made up of two DMγP·HBr·H_2O units. The following hydrogen bonding scheme is suggested:



The carbonyl C–O distance is 1.32 Å, the O...O distance 2.53 Å, and O...Br 3.24 Å.

The preparation of crystals of 2,6-dimethyl-γ-pyrone hydrobromide monohydrate, DMγP·HBr·H_2O, has been described in a previous communication.[1] The crystals are elongated triclinic plates, with the a axis in the direction of elongation, and the b axis approximately normal to the plate. The cell dimensions are $a = 7.00$ Å; $b = 8.33$ Å; $c = 9.47$ Å (all ± 0.03 Å); $\alpha = 109.9°$; $\beta = 92.9°$; $\gamma = 106.0°$ (all ± 0.5°).

The density, as determined by flotation, is 1.50 g cm^{-3}, the same as that calculated from the X-ray data for 2 DMγP·HBr·H_2O in the unit cell. The space group was taken to be $P\bar{1}$, an assumption which has been substantiated by the successful determination of the crystal structure.

EXPERIMENTAL

Intensity data for the 0*kl* and *h*0*l* zones were obtained from integrated Weissenberg photographs taken with Ni-filtered Cu radiation. Since the crystals are hygroscopic, they were kept in sealed capillaries during the exposures. The crystal used for the 0*kl* data was a prism 0.2 mm long with a cross section of about 0.07 mm × 0.1 mm, while that for the *h*0*l* data was a square plate with dimensions 0.08 mm × 0.08 mm × 0.03 mm. The intensities were measured with a photometer and the usual Lorentz and polarization corrections were applied. No absorption or extinction corrections were made. However, some low order reflections, particularly in the 0*kl* zone, apparently come out too weak. In the 0*kl* zone 174 of 186 possible reflections were observed, and in the *h*0*l* zone 133 of 150.

SOLUTION OF THE STRUCTURE

The structure was solved in two projections by use of sharpened Patterson syntheses. The sharpening was achieved by multiplying each F^2 term by the corresponding value of $(\Sigma f_i)^{-2}$. From the 0*kl* Patterson synthesis approximate y and z parameters for bromine and all the heavy atoms in the DM*y*P molecule could be deduced. The presence of one molecule of water was also clearly indicated. The parameters were refined through a series of Fourier and difference Fourier syntheses, and finally through three cycles of full matrix least-squares refinement. The temperature factors were taken to be isotropic, except for Br, for which an anisotropic temperature factor was introduced.

The x,z projection was solved and refined in a similar way.

Unobserved reflections, and some low order reflections, marked with U and N respectively in Table 3, were not included in the least-squares refinements. No hydrogen atoms were included in the calculations.

The final parameters arrived at are given in Table 1. A comparison of observed and calculated structure factors is given in Table 3. The final R factor is 0.11 for the 0*kl* zone and 0.076 for the *h*0*l* zone, not including unobserved reflections.

Table 1. Final positional and thermal parameters.

Atom	x	y	z	B(0*kl*)	B(*h*0*l*
O(1)	0.8362	0.7504	0.3074	4.40	4.68
C(2)	0.8077	0.6584	0.1567	4.75	5.46
C(3)	0.7398	0.4769	0.0907	4.36	5.01
C(4)	0.6997	0.3811	0.1894	4.29	5.36
C(5)	0.7350	0.4812	0.3450	4.33	4.46
C(6)	0.8020	0.6571	0.4051	4.90	4.09
C(7)	0.8503	0.7824	0.5651	5.95	6.12
C(8)	0.8563	0.7846	0.0670	5.45	10.3
O(9)	0.6318	0.2036	0.1250	4.82	6.77
O(10)	0.5921	0.0548	0.3185	5.03	7.33
Br(11)	0.3059	0.6816	0.3257	—	—

For Br(11) 0*kl* $b_{22} = 0.02539$ $b_{33} = 0.01369$ $b_{23} = 0.01373$
*h*0*l* $b_{11} = 0.0279$ $b_{33} = 0.0127$ $b_{13} = 0.00356$

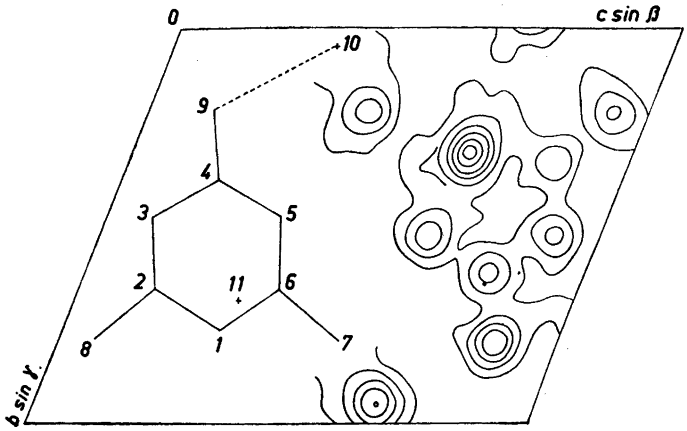


Fig. 1. Projection of the structure along the *a* axis. Contour lines for Br at 2, 10, 20, ...eÅ^{-2}, for other atoms at 2, 4, 6...eÅ^{-2}. The numbering system adopted is shown.

The standard deviations in atomic positions as estimated from the inverse of the least-squares normal equation matrices are about 0.003 Å for the bromine and between 0.02 Å and 0.03 Å for the other atoms. Due to overlap of bromine with O(1) and C(6) in the *yz* projection, the positions found for these two ring atoms are probably less reliable than the others.

DESCRIPTION OF THE STRUCTURE

Fig. 1. shows a projection of the structure along the *a* axis. The numbering system adopted is also indicated. The structure consists of centrosymmetric groups made up of two formula units of DMγP·HBr·H_2O. The central part of one group is a parallelogram with the corners occupied by two Br atoms and two water oxygen atoms. The pyrone molecules are attached to the water oxygens through strong hydrogen bonds from the keto groups. The bromine atoms in one molecular layer are situated near the line of connection between

Table 2. Observed distances and angles in DMγP·HBr·H_2O

Distances (in Å)		Angles (in degrees)	
O(1) – C(2)	1.34	O(1)–C(2)–C(3)	124.2
O(1) – C(6)	1.39	C(2)–C(3)–C(4)	116.7
C(2) – C(3)	1.35	C(3)–C(4)–C(5)	117.4
C(3) – C(4)	1.41	C(4)–C(5)–C(6)	124.4
C(4) – C(5)	1.39	C(5)–C(6)–O(1)	118.0
C(5) – C(6)	1.31	C(2)–O(1)–C(6)	119.3
C(6) – C(7)	1.48	C(1)–C(2)–C(8)	111.9
C(2) – C(8)	1.54	C(1)–C(6)–C(7)	110.8
C(4) – O(9)	1.32	C(3)–C(4)–O(9)	116.8
O(9)...O(10)	2.53	C(4)–O(9)–O(10)	112.4
O(10)...Br(11)′	3.25	Br(11)′–O(10)–Br(11)″	103.0
O(10)...Br(11)″	3.23	(Br(11)′ at: 0.6941, 0.3184, 0.6743)	
		(Br(11)″ at: 0.3059, –0.3184, 0.3257)	

Table 3. Observed and calculated structure factors. Reflections marked with N or U were not included in the least-squares calculations. F_o for unobserved reflections, marked with U, correspond to the minimum observable.

$h = 0$

k	l	F_o	F_c	k	l	F_o	F_c	k	l	F_o	F_c
0	1	27.3N	−27.4	2	9	1.9	−1.6	5	$\bar{4}$	17.6	16.8
0	2	39.8N	−47.4	2	$\bar{10}$	5.5	−5.0	5	$\bar{3}$	21.7	−23.6
0	3	51.7N	56.3	3	$\bar{12}$	2.7	3.1	5	$\bar{2}$	1.6U	0.2
0	4	38.7	−36.6	3	$\bar{11}$	8.6	−8.0	5	$\bar{1}$	30.7	31.0
0	5	33.0	−34.7	3	$\bar{10}$	2.8	2.8	5	0	15.4	−15.1
0	6	28.3	29.4	3	$\bar{9}$	2.0	1.7	5	1	2.9	−2.5
0	7	1.9U	−1.4	3	$\bar{8}$	20.4	−21.0	5	2	19.3	19.0
0	8	17.6	−17.8	3	$\bar{7}$	14.2	14.4	5	3	21.2	−19.2
0	9	11.7	11.7	3	$\bar{6}$	30.6	30.3	5	4	2.5	−1.8
0	10	1.6	0.8	3	$\bar{5}$	19.8	−20.3	5	5	11.0	10.9
0	11	5.2	−5.6	3	$\bar{4}$	22.5	24.2	5	6	4.2	−4.6
1	$\bar{11}$	4.0	4.2	3	$\bar{3}$	26.5	25.6	5	7	1.3U	−0.6
1	$\bar{10}$	7.2	−7.0	3	$\bar{2}$	46.9N	−54.5	6	$\bar{11}$	3.6	−3.8
1	$\bar{9}$	3.2	2.6	3	$\bar{1}$	2.0U	0.9	6	$\bar{10}$	4.6	4.6
1	$\bar{8}$	11.7	11.4	3	0	30.6	36.7	6	$\bar{9}$	4.6	4.1
1	$\bar{7}$	16.9	−17.0	3	1	41.5	−49.8	6	$\bar{8}$	7.4	−7.1
1	$\bar{6}$	5.8	−5.5	3	2	11.3	−12.7	6	$\bar{7}$	6.3	6.2
1	$\bar{5}$	26.3	24.5	3	3	34.3	32.5	6	$\bar{6}$	5.0	4.6
1	$\bar{4}$	38.7	−36.7	3	4	19.8	−20.9	6	$\bar{5}$	14.9	−15.6
1	$\bar{3}$	1.1U	−1.5	3	5	2.0	− 1.4	6	$\bar{4}$	5.8	−5.5
1	$\bar{2}$	49.2N	67.8	3	6	15.5	15.9	6	$\bar{3}$	6.8	7.3
1	$\bar{1}$	38.2N	−50.4	3	7	6.4	−6.3	6	$\bar{2}$	13.3	−14.1
1	0	28.7	−45.6	3	8	5.0	−4.3	6	$\bar{1}$	7.2	6.7
1	1	40.2N	57.4	3	9	5.2	5.7	6	0	13.3	14.5
1	2	31.0N	−36.4	4	$\bar{12}$	2.0	1.4	6	1	13.8	−13.2
1	3	23.2	−19.8	4	$\bar{11}$	5.0	4.1	6	2	2.0U	1.1
1	4	49.0	51.9	4	$\bar{10}$	11.3	−10.4	6	3	8.4	8.3
1	5	16.2	−14.4	4	$\bar{9}$	5.5	5.6	6	4	6.7	−6.4
1	6	13.7	−12.1	4	$\bar{8}$	9.5	8.3	6	5	1.5U	0.7
1	7	20.1	21.1	4	$\bar{7}$	16.5	−14.8	6	6	5.4	4.7
1	8	2.0U	−0.7	4	$\bar{6}$	6.0	5.4	7	$\bar{11}$	2.5	2.5
1	9	7.8	−7.8	4	$\bar{5}$	11.9	11.2	7	$\bar{10}$	4.4	−4.5
1	10	4.3	5.0	4	$\bar{4}$	17.0	−19.2	7	$\bar{9}$	3.1	2.5
2	$\bar{11}$	3.2	2.7	4	$\bar{3}$	3.9	2.5	7	$\bar{8}$	3.8	3.6
2	$\bar{10}$	10.2	9.9	4	$\bar{2}$	21.7	24.1	7	$\bar{7}$	9.2	−10.2
2	$\bar{9}$	9.9	−9.4	4	$\bar{1}$	31.8	−35.5	7	$\bar{6}$	2.0U	0.9
2	$\bar{8}$	6.4	5.6	4	0	8.0	8.1	7	$\bar{5}$	9.1	7.7
2	$\bar{7}$	11.0	10.4	4	1	31.4	31.6	7	$\bar{4}$	2.0	1.1
2	$\bar{6}$	27.3	−28.4	4	2	12.6	−12.5	7	$\bar{3}$	4.0	4.3
2	$\bar{5}$	9.1	−8.9	4	3	8.0	8.0	7	$\bar{2}$	7.8	6.8
2	$\bar{4}$	35.5	39.2	4	4	9.8	9.7	7	$\bar{1}$	9.0	−8.8
2	$\bar{3}$	15.8N	−15.4	4	5	16.5	−16.5	7	0	7.5	−7.7
2	$\bar{2}$	30.8N	−29.6	4	6	6.8	−5.9	7	1	5.0	4.6
2	$\bar{1}$	44.5N	63.4	4	7	5.8	5.3	7	2	5.5	−5.3
2	0	41.3N	−53.9	4	8	2.9	−2.8	7	3	1.7U	−0.1
2	1	28.7N	−32.3	5	$\bar{12}$	5.0	−6.1	7	4	2.8	3.1
2	2	39.4	46.1	5	$\bar{11}$	1.5	1.1	7	5	2.3	−2.2
2	3	18.0	−18.4	5	$\bar{10}$	6.8	6.3	8	$\bar{10}$	1.9	1.5
2	4	11.9	−13.0	5	$\bar{9}$	10.6	−10.6	8	$\bar{9}$	6.3	−6.4
2	5	25.7	27.4	5	$\bar{8}$	3.2	3.7	8	$\bar{8}$	4.7	4.6
2	6	2.0U	−1.0	5	$\bar{7}$	13.1	12.7	8	$\bar{7}$	3.8	3.5
2	7	13.3	−12.3	5	$\bar{6}$	21.8	−22.0	8	$\bar{6}$	5.9	−5.4
2	8	8.0	8.4	5	$\bar{5}$	1.7	1.6	8	$\bar{5}$	4.8	4.6

k	l	F_o	F_c	h	l	F_o	F_c	h	l	F_o	F_c
8	$\bar{4}$	5.4	4.7	2	$\bar{11}$	5.1	5.6	4	5	13.0	12.9
8	$\bar{3}$	9.1	−8.8	2	$\bar{10}$	4.3	−5.3	4	6	8.2	7.0
8	$\bar{2}$	1.9U	1.2	2	$\bar{9}$	3.6	−4.0	4	7	11.5	−12.6
8	$\bar{1}$	5.2	4.9	2	$\bar{8}$	14.0	14.5	4	$\bar{8}$	2.8	2.5
8	0	5.4	−5.1	2	$\bar{7}$	9.2	−9.6	5	$\bar{10}$	2.0U	−0.1
8	1	1.7	0.6	2	$\bar{6}$	16.8	−16.6	5	$\bar{9}$	6.1	−6.1
8	2	2.9	2.8	2	$\bar{5}$	26.8	27.5	5	$\bar{8}$	8.9	9.5
8	3	2.4	−2.7	2	$\bar{4}$	10.7	−8.3	5	$\bar{7}$	3.8	3.6
9	$\bar{9}$	0.9U	0.1	2	$\bar{3}$	23.7	−23.0	5	$\bar{6}$	12.0	−12.9
9	$\bar{8}$	5.4	−5.4	2	$\bar{2}$	48.4	52.7	5	$\bar{5}$	9.9	9.8
9	$\bar{7}$	3.8	4.4	2	$\bar{1}$	6.9	−7.7	5	$\bar{4}$	3.8U	1.1
9	$\bar{6}$	2.4	2.3	2	0	71.4	−79.7	5	$\bar{3}$	19.6	−18.8
9	$\bar{5}$	4.4	−4.3	2	1	36.0	38.7	5	$\bar{2}$	15.8	16.5
9	$\bar{4}$	1.7	2.3	2	2	4.6	−4.4	5	$\bar{1}$	5.6	5.0
9	$\bar{3}$	1.7	2.0	2	3	32.6	−35.0	5	0	16.1	−14.9
9	$\bar{2}$	3.1	−2.8	2	4	41.3	40.9	5	1	7.9	8.8
9	$\bar{1}$	1.5	1.4	2	5	3.3U	2.8	5	2	6.1	4.8
9	0	3.1	2.9	2	6	18.6	−18.6	5	3	13.0	−12.7
9	1	2.7	−2.6	2	7	13.3	13.8	5	4	4.8	4.2
10	$\bar{6}$	1.1U	0.5	2	8	6.1	6.0	5	5	7.7	6.3
10	$\bar{5}$	2.8	2.2	2	9	9.9	−10.0	5	6	8.7	−8.4
10	$\bar{4}$	4.0	−4.1	2	10	3.3	3.9	5	7	3.8	4.1
10	$\bar{3}$	1.1U	0.0	3	$\bar{11}$	2.8	−2.3	6	$\bar{9}$	2.8	3.0
				3	$\bar{10}$	5.4	−5.2	6	$\bar{8}$	2.8U	−1.8
$k = 0$				3	$\bar{9}$	11.5	10.6	6	$\bar{7}$	3.3	−3.3
h	l			3	$\bar{8}$	3.8	−3.3	6	$\bar{6}$	7.4	7.9
0	1	31.1N	−27.7	3	$\bar{7}$	16.1	−16.1	6	$\bar{5}$	3.8	4.1
0	2	45.4N	−47.5	3	$\bar{6}$	27.0	26.6	6	$\bar{4}$	8.9	−8.8
0	3	57.1	56.5	3	$\bar{5}$	6.1	−6.2	6	$\bar{3}$	5.4	3.9
0	4	40.5	−35.7	3	$\bar{4}$	31.6	−30.3	6	$\bar{2}$	5.4	5.6
0	5	35.4	−33.2	3	$\bar{3}$	32.4	31.5	6	$\bar{1}$	14.0	−15.5
0	6	30.3	29.8	3	$\bar{2}$	5.9	−6.6	6	0	8.9	8.5
0	7	2.3U	−1.2	3	$\bar{1}$	22.7	−21.0	6	1	6.1	6.8
0	8	19.1	−17.3	3	0	23.2	23.9	6	2	12.7	−12.7
0	9	12.5	12.2	3	1	6.9	8.3	6	3	4.6	4.8
0	10	3.1U	0.8	3	2	30.1	−34.0	6	4	5.6	5.0
0	11	6.1	−6.0	3	3	13.8	14.5	6	5	6.6	−6.7
1	$\bar{11}$	2.3U	−1.5	3	4	8.4	8.3	6	6	3.3	0.8
1	$\bar{10}$	8.9	8.6	3	5	19.1	−20.7	7	$\bar{7}$	3.6	1.9
1	$\bar{9}$	8.4	−7.4	3	6	10.7	10.9	7	$\bar{6}$	4.1	3.0
1	$\bar{8}$	5.4	−6.3	3	7	3.8U	2.0	7	$\bar{5}$	6.6	−7.7
1	$\bar{7}$	20.9	20.5	3	8	7.7	−8.2	7	$\bar{4}$	6.1	6.4
1	$\bar{6}$	19.4	−17.7	3	9	5.4	5.8	7	$\bar{3}$	5.1	6.7
1	$\bar{5}$	4.1	0.8	4	$\bar{10}$	6.4	6.5	7	$\bar{2}$	8.9	−9.3
1	$\bar{4}$	30.6	32.5	4	$\bar{9}$	3.3	−3.4	7	$\bar{1}$	3.6U	2.4
1	$\bar{3}$	37.0	−34.5	4	$\bar{8}$	3.8	−4.4	7	0	7.4	7.0
1	$\bar{2}$	34.2N	−33.7	4	$\bar{7}$	9.2	9.8	7	1	7.1	−8.0
1	$\bar{1}$	5.6N	−5.3	4	$\bar{6}$	4.8	−4.9	7	2	3.3U	1.0
1	0	17.8N	−21.9	4	$\bar{5}$	16.3	−15.5	7	3	5.1	5.1
1	1	14.0N	11.1	4	$\bar{4}$	25.5	25.3	7	4	5.6	−5.9
1	2	62.5N	72.2	4	$\bar{3}$	3.3U	0.1	8	$\bar{5}$	2.3U	1.2
1	3	2.8	1.5	4	$\bar{2}$	29.6	−30.9	8	$\bar{4}$	3.3	0.9
1	4	14.8	−15.5	4	$\bar{1}$	29.6	30.8	8	$\bar{3}$	3.6	−3.5
1	5	18.6	21.8	4	0	3.1U	−1.0	8	$\bar{2}$	2.8U	2.3
1	6	8.4	−6.1	4	1	29.8	−32.3	8	$\bar{1}$	3.8	3.1
1	7	15.8	−14.0	4	2	21.4	23.9	8	0	4.8	−5.1
1	8	12.0	11.4	4	3	7.4	6.8	8	1	2.3U	2.2
1	9	3.6U	−1.9	4	4	23.2	−23.0	8	2	3.1	3.8
1	10	7.4	−7.4								

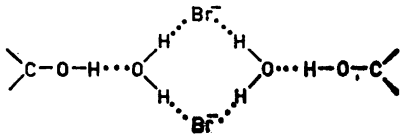
one ring oxygen and the corresponding atom, one translational period away along *a*.

The least-squares plane calculated from the positional parameters of the pyrone molecule has the equation

$$(0.1417\mathbf{a} - 0.0038\mathbf{b} + 0.0053\mathbf{c}) \cdot \mathbf{r} - 3.8838 = 0$$

i.e. the molecules are situated in planes very nearly normal to the *a* axis. Interatomic distances and angles are given in Table 2. Of particular interest is the C(4)—O(9) distance of 1.32 Å, which is considerably longer than the corresponding distance of 1.245 Å found in the free DMγP molecule,[2] an observation which is taken to indicate that a proton has been added to the keto oxygen. This should give rise to a more benzenoid ring. The distances C(3)—C(4) and C(4)—C(5) also give some support to this idea. However, as is clearly indicated by the values found for some other distances, the accuracy of the present data does not justify a detailed discussion of the ring structure.

Of interest is also the short hydrogen bonded distance O(9)—O(10) of 2.53 Å. Based on the assumption that a proton has been transferred to the keto oxygen, the following hydrogen bonding scheme is suggested:



It appears to be of interest to investigate more thoroughly some aspects of the structure than is possible with two-dimensional methods. Three-dimensional analyses of both the hydrobromide monohydrate and the corresponding hydrochloride will be undertaken.

The author gratefully acknowledges the financial support of part of this study through a grant from *Alf Bjerckes Legat*.

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Received October 30, 1964.