

Synthesis, Characterization, and Crystal Structure of the Lactone Form of Rhodamine B

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Perfect single crystals of a lactone form of rhodamine B (RB lactone, 3', 6'-bis(di-ethylamino)-spiro-[isobenzofuran-1(3H), 9'-[9H]xanthene]-3-one, C₂₈H₃₀N₂O₃) were hydrothermally prepared in a sol-gel system of rhodamine B–Na₂O–SiO₂–glycerol–H₂O. The product of crystalline RB lactone was identified by ¹H NMR. The structure was determined by single-crystal X-ray diffraction. Lactone crystallizes in a monoclinic system, space group *P*2₁/*n* with *a* = 16.559(3) Å, *b* = 15.657(3) Å, *c* = 19.381(2) Å, β = 100.10(1)°, *V* = 4947(1) Å³, *Z* = 8. The structure was resolved by direct method and refined to *R* = 0.060 and *R*_w = 0.064 on the basis of 3834 observed reflections with *I* > 2.50σ(*I*). An asymmetric unit consists of two independent lactone molecules. Both molecules contain a central planar section and planar groups bonded to the central carbon, respectively. Pure phase of the lactone crystallites obtained was confirmed by comparison of the observed XRD pattern with the simulated one.

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Key Words: Rhodamine B; lactone; synthesis; sol-gel method; crystal structure; ¹H NMR; XRD.

INTRODUCTION

Rhodamine B (RB) is a xanthene dye usually used as an active medium for tuning lasers (1). Recently, it has found a wide application as biological stain (2), water tracing agent (3), electrochemical luminescence sensitizer (4), molecular probe (5), and solar collector (6), etc. Therefore, to meet the need of the applications clear characterization of the structure and the properties of RB has attracted considerable attention.

The equilibrium between the two forms of RB, the colored zwitterion and the colorless lactone (RB lactone, 3', 6'-bis(di-ethylamino)-spiro[isobenzofuran-1(3H), 9'-[9H]xanthene]-3-one, C₂₈H₃₀N₂O₃), shown in Fig. 1, has been known for a long time (7). Needles of RB lactone, which

were identified only by ¹H NMR, UV, and IR spectra, can be prepared from the zwitterion form by the methods reported by Barra *et al.* (8) and Klein *et al.* (9). Although so many rhodamine compounds and derivatives have been obtained, there are only three previous reports about the determination of the crystal structure for rhodamine derivatives (10–12). Hitherto no structural analysis of the lactone form of rhodamine B by X-ray single-crystal diffraction has been published.

In this paper, we report the preparation of the single crystals of RB lactone and its first detailed crystal structure analysis. The characterization of the crystalline product of RB lactone with ¹H NMR and X-ray powder diffraction is reported as well.

EXPERIMENTAL

Preparation of RB Lactone

RB lactone was hydrothermally synthesized from a mixture of rhodamine B (*N*-[9-(2-carboxyphenyl)-6-(diethylamino)-3H-xanthene-3-ylidene]-*N*-ethylethanamium chloride, Fluka), silica sol (22 wt% SiO₂, 0.2 wt% Na₂O), aqueous solution of NaOH (10%), glycerol, and distilled water. In a typical preparation, an aqueous solution of NaOH (2.665 g) was added into silica sol (5.455 g) by stirring until a homogeneous mixture formed. Then a mixture of rhodamine B (1.916 g), glycerol (16.26 g), and distilled water (10 ml) was added. A red homogeneous sol of a reactant was obtained after vigorous stirring for 1 h at ambient temperature. The molar composition of the reactant was 0.2 RB:0.18 Na₂O:1.0 SiO₂:10 glycerol:40 H₂O. The sol was sealed in a stainless steel autoclave lined with Teflon and reacted under autogeneous pressure at 100°C for 2 days. A gel was formed from the sol after being heated for several hours at the reaction temperature. Single crystals of RB lactone up to millimeter sizes with slightly red color were crystallized in the gel, and easily separated from the gel and then dried at 60°C for 2 h.

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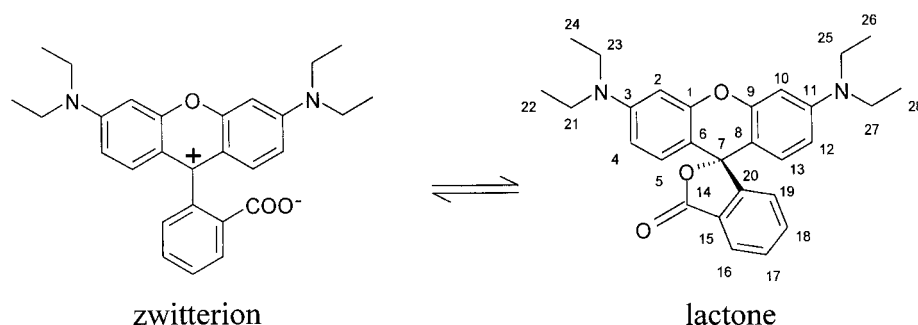


FIG. 1. The equilibrium between the zwitterion and the lactone forms of rhodamine B in solution.

Identification and Characterization

The morphology and the size of single crystals obtained were observed with an AO Micro Star optical microscopy. XRD patterns of the crystals were measured with a Rigaku D MAX/II A X-ray powder diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm) in the 2θ range of $2\text{--}50^\circ$ at a scanning speed of $8^\circ/\text{min}$. The simulated XRD pattern was obtained with PowderCell program (13) according to the data of lactone crystal structure. ^1H NMR spectrum was recorded on a JNM-PMX 60SI spectrometer with tetramethyl silicane (TMS) as the reference.

Crystal Structure Determination

A single crystal of RB lactone with dimensions of $0.20 \times 0.20 \times 0.30$ mm was mounted in a glass capillary. All

TABLE 1
Summary of Crystal Data for RB Lactone

Formula	$\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_3$
M_r	442.55
Crystal color, habit	Slightly red, prismatic
Crystal system	Monoclinic
Space group	$P2_1/n$
a (nm)	1.6559(3)
b (nm)	1.5657(3)
c (nm)	1.9381(2)
β ($^\circ$)	100.10(1)
V (nm^3)	4.947(1)
Z	8
D_c (g cm^{-3})	1.188
μ (mm^{-1})	0.077
$F(000)$	1888.0
T (K)	293(1)
Max. 2θ	50.0
No. of unique reflections	9063
No. of observed reflections	3834 ($I > 2.50\sigma(I)$)
Parameters refined	595
R	0.060
R_w	0.064
S (goodness of fit)	1.91
Largest diffraction peak and hole (e nm^{-3})	260 to -230

measurements were made on a Rigaku AFC7R diffractometer with a 12-kW rotating anode generator and graphite monochromated $\text{MoK}\alpha$ radiation, $\lambda = 0.071069$ nm. The data were collected at a temperature of 293 (1) K using the ω - 2θ scan technique to a maximum 2θ value of 50.0° . An empirical absorption correction based on azimuthal scans of several reflections was applied, resulting in transmission factors ranging from 0.98 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 1.0455×10^{-7}). The structure was elucidated by direct methods (14) and expanded using Fourier technique (15). The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were also applied throughout this work. All calculations were performed using teXsan (16) crystallographic software package of Molecular Structure Corporation. Crystal data, data collection, and refinement results are summarized in Table 1.

RESULTS AND DISCUSSION

Synthesis of RB Lactone

The synthesis conditions and the crystallization products are listed in Table 2. It can be found that RB lactone formed

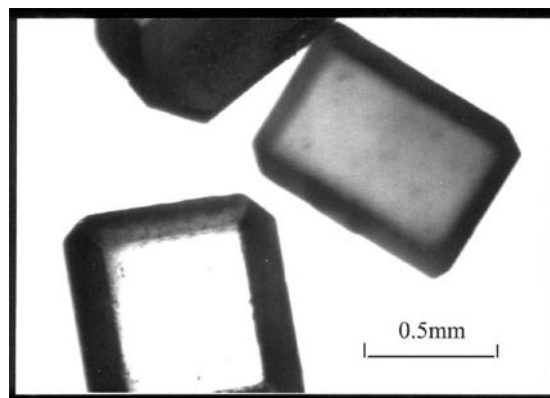


FIG. 2. Optical photograph of prismatic single crystals of RB lactone.

TABLE 2
Examples for Synthesis of RB Lactone

No.	Gel composition (molar ratio)					<i>T</i> (°C)	<i>t</i> (h)	Product	Average size of the single crystals (mm) ^b
	RB	SiO ₂	Na ₂ O	H ₂ O	GC ^a				
1	0.2	0	0.18	50	0	120	72	No crystallite	
2	0.2	0	0.18	45	5	120	72	No crystallite	
3	0.2	0	0.18	40	10	140	72	No crystallite	
4	0.2	1	0.18	50	0	120	48	Single crystal + aggregates	0.88
5	0.2	1	0.18	45	5	120	48	Perfect single crystal	1.14
6	0.2	1	0.18	40	10	120	48	Perfect single crystal	1.29
7	0.2	1	0.18	35	15	120	48	No crystallite	
8	0.2	1	0.18	45	5	70	48	No crystallite	
9	0.2	1	0.18	45	5	80	48	Aggregates	
10	0.2	1	0.18	45	5	100	48	Perfect single crystal	0.73
11	0.2	1	0.18	45	5	140	48	Perfect single crystal	1.17
12	0.2	1	0.18	45	5	160	48	No crystallite	

^aGC, glycerol.

^bThe average size of the single crystals is the average length of diagonal for 50 single crystals.

TABLE 3
Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å²) for Nonhydrogen Atoms for the Lactone Form of Rhodamine B

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} ^a
O(1)	0.7490(2)	0.6385(2)	0.1321(2)	0.0655	O(2)	0.9660(2)	0.5611(2)	0.4119(2)	0.0957
O(3)	0.8881(2)	0.5899(2)	0.3086(2)	0.0582	O(4)	0.6061(2)	0.4364(2)	− 0.2962(2)	0.0680
O(5)	0.7173(2)	0.1337(2)	− 0.1060(2)	0.0827	O(6)	0.6751(2)	0.2444(2)	− 0.1756(2)	0.0636
N(1)	0.8225(3)	0.9298(2)	0.1351(2)	0.0742	N(2)	0.6513(2)	0.3542(2)	0.0999(2)	0.0641
N(3)	0.7275(3)	0.6401(3)	− 0.1275(3)	0.0837	N(4)	0.4626(4)	0.2669(4)	− 0.4800(3)	0.1162
C(1)	0.8074(3)	0.6984(3)	0.1589(2)	0.0519	C(2)	0.7884(3)	0.7809(3)	0.1356(3)	0.0603
C(3)	0.8421(3)	0.8483(3)	0.1574(3)	0.0571	C(4)	0.9161(3)	0.8280(3)	0.2025(3)	0.0621
C(5)	0.9321(3)	0.7453(3)	0.2246(2)	0.0575	C(6)	0.8785(3)	0.6777(3)	0.2034(2)	0.0484
C(7)	0.8942(3)	0.5884(3)	0.2313(2)	0.0499	C(8)	0.8314(3)	0.5276(3)	0.1963(2)	0.0481
C(9)	0.7632(3)	0.5531(3)	0.1500(2)	0.0498	C(10)	0.7025(3)	0.4985(3)	0.1174(2)	0.0534
C(11)	0.7093(3)	0.4105(3)	0.1320(2)	0.0529	C(12)	0.7777(3)	0.3830(3)	0.1805(3)	0.0613
C(13)	0.8361(3)	0.4398(3)	0.2108(2)	0.0589	C(14)	0.9588(3)	0.5651(3)	0.3488(3)	0.0624
C(15)	1.0182(3)	0.5462(3)	0.3032(3)	0.0554	C(16)	1.0992(4)	0.5184(3)	0.3216(3)	0.0749
C(17)	1.1414(3)	0.5039(4)	0.2682(4)	0.0896	C(18)	1.1057(4)	0.5158(4)	0.1987(4)	0.0894
C(19)	1.0245(3)	0.5426(3)	0.1813(3)	0.0723	C(20)	0.9813(3)	0.5588(3)	0.2353(2)	0.0497
C(21)	0.8801(3)	1.0005(3)	0.1503(3)	0.0700	C(22)	0.8707(4)	1.0463(4)	0.2169(3)	0.0996
C(23)	0.7405(4)	0.9508(3)	0.0987(4)	0.0950	C(24)	0.7300(5)	0.9465(5)	0.0215(4)	0.1488
C(25)	0.5791(3)	0.3809(3)	0.0526(3)	0.0655	C(26)	0.5095(4)	0.4031(4)	0.0893(3)	0.1044
C(27)	0.6573(3)	0.2632(3)	0.1178(3)	0.0716	C(28)	0.7166(4)	0.2158(3)	0.0804(3)	0.0922
C(29)	0.6347(3)	0.4534(3)	− 0.2258(3)	0.0548	C(30)	0.6643(3)	0.5354(3)	− 0.2124(3)	0.0629
C(31)	0.6965(3)	0.5600(3)	− 0.1432(3)	0.0624	C(32)	0.6966(3)	0.4987(3)	− 0.0907(3)	0.0630
C(33)	0.6660(3)	0.4182(3)	− 0.1062(2)	0.0609	C(34)	0.6335(3)	0.3928(3)	− 0.1743(2)	0.0508
C(35)	0.6021(3)	0.3041(3)	− 0.1907(2)	0.0530	C(36)	0.5641(3)	0.2950(3)	− 0.2660(2)	0.0524
C(37)	0.5695(3)	0.3582(3)	− 0.3142(2)	0.0579	C(38)	0.5376(3)	0.3502(3)	− 0.3845(3)	0.0685
C(39)	0.4952(3)	0.2766(4)	− 0.4098(3)	0.0752	C(40)	0.4891(3)	0.2125(3)	− 0.3617(3)	0.0789
C(41)	0.5222(3)	0.2210(3)	− 0.2920(3)	0.0704	C(42)	0.6648(3)	0.1858(3)	− 0.1258(3)	0.0617
C(43)	0.5850(3)	0.2011(3)	− 0.1054(2)	0.0535	C(44)	0.5477(4)	0.1567(3)	− 0.0574(3)	0.0670
C(45)	0.4729(4)	0.1861(4)	− 0.0462(3)	0.0772	C(46)	0.4368(3)	0.2573(4)	− 0.0817(3)	0.0732
C(47)	0.4738(3)	0.3006(3)	− 0.1296(3)	0.0600	C(48)	0.5494(3)	0.2705(3)	− 0.1409(2)	0.0500
C(49)	0.7532(5)	0.6692(4)	− 0.0542(4)	0.1045	C(50)	0.8393(5)	0.6480(6)	− 0.0251(4)	0.1471
C(51)	0.7416(4)	0.6986(4)	− 0.1828(4)	0.0959	C(52)	0.6727(5)	0.7557(5)	− 0.2079(5)	0.1703
C(53)	0.4853(6)	0.3285(6)	− 0.5337(4)	0.1486	C(54)	0.4300(6)	0.3971(8)	− 0.5463(5)	0.1927
C(55)	0.4140(1)	0.1928(8)	− 0.5043(6)	0.2927	C(56)	0.399(2)	0.145 (1)	− 0.5277(9)	0.4232

^a*B*_{eq} is defined as $B_{eq} = \frac{8}{3} \pi^2 [(U_{11} (aa^*)^2 + U_{22} (bb^*)^2 + U_{33} (cc^*)^2 + 2 U_{12} aa^*bb^* \cos \gamma + 2 U_{13} aa^*cc^* \cos \beta + 2 U_{23} bb^*cc^* \cos \alpha)]$.

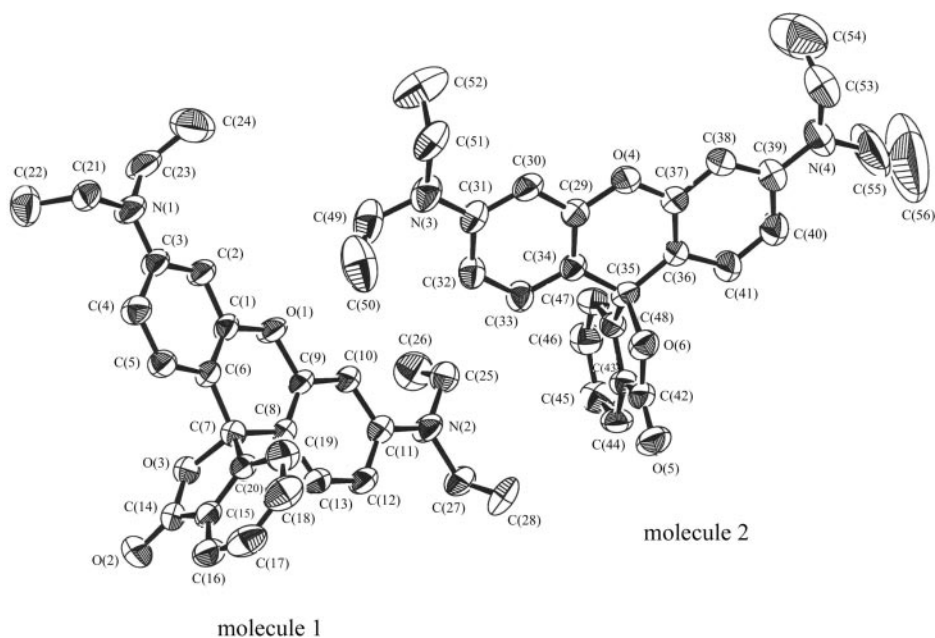


FIG. 3. A perspective view of the crystal structure (50% probability ellipsoids) with the numbering scheme, excluding H atoms. An asymmetric unit consists of two independent molecules.

only in the medium of silica gel. However, no crystalline product of RB lactone was obtained in the reactant absence of silica gel. Moreover, the glycerol content in the gel plays an important role in the growth of large perfect single crystals. The viscosity of the medium increased gradually with increasing the content of glycerol, which led to the growth of the perfect single crystals up to the size of 1 mm. However, no crystalline RB lactone could grow in a very viscous medium when the molar ratio of glycerol/H₂O = 15/35. Additionally, crystallization is also dependent on the reaction temperature. RB lactone crystallized only in the temperature range of 80–140°C.

TABLE 4
Dihedral Angle (°) for RB Lactone

Plane	1	2	3	1'	2'
2	89.77				
3	89.04	0.77			
1'	42.29	93.09	92.73		
2'	116.61	43.42	44.10	91.43	
3'	115.84	44.60	45.26	89.74	2.00

Note. Plane 1, containing O(1), N(1), N(2), and C(1)–C(13) atoms; plane 2, containing C(7), O(2), O(3), C(14), C(15), C(20) atoms; plane 3, containing C(15)–C(20) atoms; plane 1', containing O(4), N(3), N(4), and C(29)–C(41) atoms; plane 2', containing O(6), C(35), C(42), C(43), C(44) atoms; plane 3', containing C(43)–C(48) atoms.

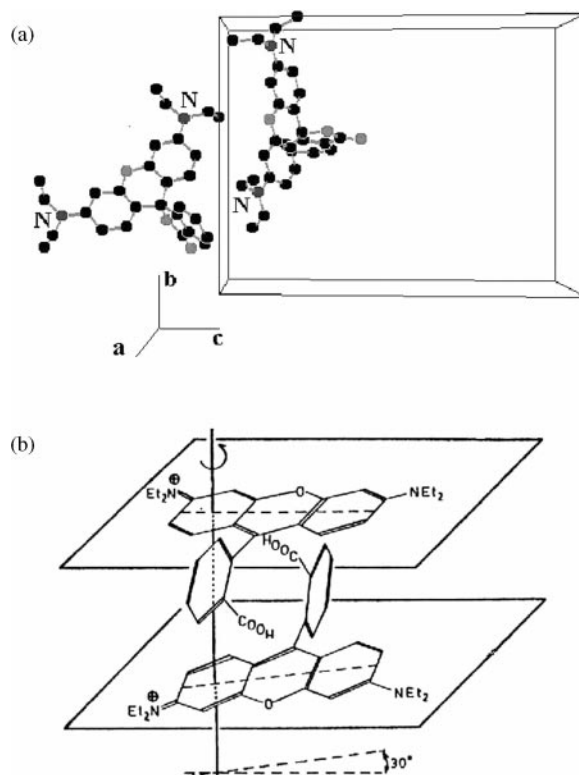


FIG. 4. Stereo view (a) of dimer of RB lactone in an asymmetric unit, with the two xanthene planes inclined 42.3° to each other, and (b) of the proposed model for the cationic dimer of RB (RBH⁺)₂ based on space-filling construction derived from Ref. (18).

TABLE 5
Selected Bond Angle ($^{\circ}$) for RB Lactone

O(3)–C(7)–C(6)	107.7(3)	C(6)–C(7)–C(8)	111.6(3)
O(3)–C(7)–C(8)	107.3(3)	C(6)–C(7)–C(20)	114.1(3)
O(3)–C(7)–C(20)	100.6(3)	C(8)–C(7)–C(20)	114.5(3)
O(6)–C(35)–C(34)	107.2(3)	C(34)–C(35)–C(36)	115.3(4)
O(6)–C(35)–C(36)	108.3(4)	C(34)–C(35)–C(48)	114.0(4)
O(6)–C(35)–C(48)	101.2(3)	C(36)–C(35)–C(48)	113.7(4)

It is obvious that silica gel and glycerol lower the diffusion of soluble species in the reactant, preventing the formation of mass nuclei of RB lactone. In this situation, the crystals of RB lactone can grow on the fewer nuclei that formed and isolated from each other in the gel, yielding the large perfect single crystals.

Morphology

Optical microscope photograph (see Fig. 2) shows prismatic single crystals of RB lactone prepared in the sol-gel system. On investigation by an optical microscope with crossed Nicols and a gypsum plate inserted, a strong birefringence of the crystals of RB lactone was observed.

^1H NMR Spectrum

The ^1H NMR chemical shifts of RB lactone are as follows: δ_{H} (CD_3COCD_3 , ppm): 1.14 (12H, m, 22- CH_3 , 24- CH_3 , 26- CH_3 , 28- CH_3), 3.40 (8H, m, 21- CH_2 , 23- CH_2 , 25- CH_2 , 27- CH_2), 6.42 (2H, d, 4-CH, 12-CH), 6.46 (2H, d,

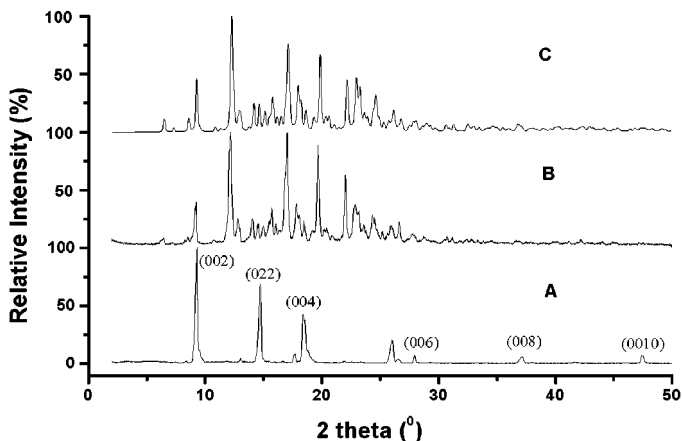


FIG. 5. XRD patterns of (A) as-synthesized single crystals, (B) powder crystallites after grinding from crystalline product obtained, and (C) the simulated with Powder Cell program (13).

TABLE 6
X-ray Powder Diffraction Data of RB Lactone

<i>h</i>	<i>k</i>	<i>l</i>	2θ ($^{\circ}$) Observed	<i>d</i> (\AA) Observed	<i>d</i> (\AA) Calculated	I/I_0 (%) Observed
–1	0	1	6.54	13.515	13.631	9.0
0	1	1	7.27	12.144	12.104	4.9
–1	1	1	8.60	10.276	10.281	9.4
0	0	2	9.26	9.541	9.540	39.4
2	0	0	10.83	8.161	8.151	7.3
0	2	0	11.36	7.783	7.828	6.6
2	1	0	12.23	7.234	7.230	100
–2	0	2	12.91	6.853	6.816	26.0
–2	1	2	14.14	6.261	6.249	27.2
0	2	2	14.61	6.058	6.052	21.1
–1	1	3	15.07	5.873	5.854	19.4
–2	2	1	15.82	5.597	5.603	33.0
–3	0	1	16.14	5.486	5.486	21.4
2	1	2	16.47	5.378	5.374	15.6
–3	1	1	17.10	5.181	5.177	99.8
0	2	3	17.91	4.948	4.936	38.4
–1	3	1	18.13	4.889	4.874	28.5
0	0	4	18.55	4.778	4.770	23.4
–1	1	4	19.29	4.598	4.600	15.3
–2	0	4	19.76	4.488	4.473	88.3
–2	3	1	20.29	4.373	4.375	15.7
1	3	2	20.52	4.325	4.315	16.4
2	3	1	21.14	4.199	4.197	11.4
–4	0	2	22.11	4.017	4.011	63.0
–1	0	5	22.94	3.874	3.869	37.7
–3	1	4	23.22	3.827	3.825	31.7
3	3	0	23.68	3.755	3.764	20.3
4	2	0	24.48	3.634	3.615	28.1
–3	2	4	25.28	3.520	3.522	14.5
–4	0	4	26.02	3.422	3.408	19.3
–4	1	4	26.72	3.334	3.330	22.2
0	0	6	27.89	3.197	3.180	12.0
3	4	1	28.86	3.091	3.082	10.5

2-CH, 10-CH), 6.52 (2H, d, 5-CH, 13-CH), 7.22 (1H, d, 19-CH), 7.73 (2H, m, 17-CH, 18-CH), 7.96 (1H, d, 16-CH). The data are consistent with those reported (17), proving that the crystal prepared in the sol-gel system is the lactone form of rhodamine B.

Description of the Crystal Structure

Atomic coordinates of all nonhydrogen atoms of the lactone are listed in Table 3 and the ORTEP structure with the atom-numbering scheme of the lactone is shown in Fig. 3. The structure contains two independent lactone molecules with virtually identical geometry. Molecule **1** is composed of a central planar section and two planar groups bonded to the central carbon atom C(7): (i) the major central plane, consisting of the xanthene nucleus (atoms C(1)–C(13), O(1)) and the nitrogen atoms N(1), N(2) of the diethylamino substituents; (ii) the lactone plane, containing the central

carbon atom C(7) and O(2), O(3), C(14), C(15), C(20) atoms; (iii) the benzo-group, containing the ring carbon atoms C(15)–C(20). Another three equivalent planes are shown in molecule **2**. The xanthene plane and the lactone plane are perpendicular to each other in both of the two molecules (89.77° and 91.43° , respectively, Table 4). No classical hydrogen bonds are observed in the structure. The lactone C–O bonds shown in C(7)–O(3) and C(35)–O(6) with distances of 0.1518(5) and 0.1515(5) nm, respectively, are rather longer than normal C–O single bonds. All other bonds are normal.

A space-filling molecular model (18) for the cationic dimer of RB (RBH^+)₂ in aqueous solution has been constructed on the basis of calculation of adsorption spectrum. The corresponding schematic diagram is shown in Fig. 4. In the model, the two heterocyclic rings are in parallel planes and the intermolecular axis of rotation passes through the center of benzenoid portions of the two ring systems. This model shows less steric interference between the atoms and groups than C_{2h} ($\theta = 0$) model and the positively charged amino residues are situated further apart (18). A similar geometry was found in homodimers/heterodimers of RB and rhodamine 6G in aqueous solution (19) and the crystals of heavy metal salt of rhodamine B (10). Obviously, these results are different from our data in that the xanthene planes of the two molecules of RB lactone are inclined to each other with an angle of 42.29° rather than parallel to each other to form face–face separation.

The selected bond angles around the central carbon atoms, C(7) and C(35), are listed in Table 5. All of the bond angles are about 109.5° , which on one hand suggests a change in the geometry of zwitterion especially around the central carbon atoms, favoring the transformation from a sp² to a sp³ hybridized carbon in the process of lactonization. On the other hand, the carboxylate group must be directed toward the electrophilic central carbon so as to stabilize it until reaching an appropriate position to form the C–O bond of the lactone in the process of geometrical distortion (8).

XRD Patterns

The XRD patterns of as-synthesized single crystals, powder crystallites after grinding and the simulated one, are shown in Fig. 5. A strong overlapping of several reflections (e.g., 18 reflections at $23\text{--}24^\circ$) can be observed in both XRD patterns of powder and the simulated. This is a common effect especially observed in the crystal structures with large lattice constants or with smaller but very similar lattice constants (20). All of the diffraction peaks of observed XRD patterns can be indexed based on the monoclinic cell of RB lactone determined. The fact confirms that the crystalline product prepared in the sol–gel system is a pure phase of the

lactone form without mixing any other form of RB. Both observed and calculated X-ray powder diffraction data of RB lactone are listed in Table 6. The XRD pattern of the single crystals of RB lactone shows several very strong diffraction peaks mainly with index of (0 0 *l*), indicating the preferential orientation of the single crystals on the test plate for XRD measurement.

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