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Crystal Structure of Phenolphthalein

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We have studied the molecular structures of various organic dyes by the vibrational spectroscopies[1]. Our recent research interests have been focused on the inclusion phenomena of the phthalein dyes in various organic hosts. As part of our study, the X-ray analysis of 3,3-bis(4-hydroxyphenyl)-1(3H)-isobenzofuranone, better known as phenolphthalein, was undertaken. The pH dependent color change of phenolphthalein has been ascribed to a structure change from the lactone (I) to the dianionic resonating form (II), as shown in Fig. 1. Phenolphthalein shows vibrational bands characteristic of the structure (I) in the solid state. The OH stretching bands are observed at 3383, 3329 and 3291 cm^{-1} in the IR spectrum. The intense band at 1737 cm^{-1} with a shoulder peak at 1718 cm^{-1} are assigned to the C=O stretching of the lactone group. The corresponding Raman bands are observed at 1737 and 1719 cm^{-1}. Fig. 1

Crystals suitable for X-ray analysis were grown from an aqueous ethanol solution at room temperature. A colorless prism with dimensions $0.6\times 0.3\times 0.4$ mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC-5R diffractometer with a graphite monochromated Mo Kα radiation (λ= 0.71069 Å). The detailed measurement conditions and crystal data are listed in Table 1. The intensity data were collected at 23°C using the ω-2θ scan technique to a maximum 2θ of value of 55.0°. A total of 4195 reflections were collected. The intensities of three representative reflections which were measured after every 150 reflections declined by 0.49 %. A linear correction was applied to the data to account for this phenomenon. The linear absorption coefficient for Mo Kα is 0.8 cm^{-1}. An empirical absorption correction, based on azimuthal scans of several reflections, was applied, which resulted in transmission factors ranging from 0.98 to 1.00. The data were corrected for Lorentz and polarization effects. Table 1

The structure was solved by direct methods.[2] The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from a difference Fourier map and included in the full-matrix least squares refinement. The atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography, Vol. IV.[3] All calculations were performed using the program TEXSAN

crystallographic software package.[2] Selected positional parameters are listed in Table 2. Table 2
The molecular structure is shown in Fig. 2, together with the atomic labeling scheme. Fig. 2
Selected bond distances and angles are listed in Table 3. Table 3

There are two independent molecules in the asymmetric unit (Molecule 1 and Molecule 2). Fig. 3 The molecules consist essentially of three groups: an isobenzofuran ring (A) and two *para*-hydroxyphenyl rings (B and C) attached to the tetrahedral carbon atom in the five-membered lactone ring. Each of the three moieties is almost planar. The two *para*-hydroxyphenyl groups lie on opposite sides of the isobenzofuran plane. The geometry differences between the two molecules are found in the orientations of the planes. The rings B and C are inclined with respect to each other at 71.40 ° for Molecule 1 and 74.63 ° for Molecule 2. The rings B and C are also oriented with respect to the isobenzofuran ring A at 76.65 ° and 73.63°, respectively, for Molecule 1 and 75.18 ° and 70.16 °, respectively, for Molecule 2. The C-O bonds in the five-membered lactone rings, which cleave at alkaline pH, are 1.490(3) and 1.484(3) Å, respectively, for Molecule 1 and Molecule 2. They are longer than the normal lactone C-O single bond value(1.462(2) Å)[4] and shorter than the value of 1.525(3) Å found for fluorescein[5]. Fitzgerald and Gerkin has recently reported the crystal structure of phenolphthalein obtained from ethanol solution (R= 0.045, Rw= 0.097).[6] Differences between the present work and the reported result were observed mainly in the molecular geometries of the lactone moieties.

References

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4. P. Murray-Rust, J. Murray-Rust and R. F. Newton, *Acta Cryst.*, **B35**, 1918 (1979).
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Table 1 Crystal and experimental data

Formula: $C_{20}H_{14}O_4$
Formula weight: 318.33
Crystal system: orthorhombic
Space group: $Pna2_1$ Z= 8
a= 19.276(3) Å
b= 14.822(2) Å
c= 11.3884(9) Å
V= 3254(1) $Å^3$
$Dcalc$= 1.299 g/cm^3
No. of reflections used= 2970 ($I>1.20\sigma(I)$)
No. of parameters = 542
R=0.038, R_w=0.037
Goodness-of-fit = 1.25
$\Delta\rho_{max}(eÅ^{-3})/\ \Delta\rho_{min}(eÅ^{-3})$ = 0.18 / -0.18
Measurement: Rigaku AFC-5R
Program system: TEXSAN
Structure determination: direct method
Refinement: full-matrix least-squares

Table 2 Fractional coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms

Atom	x	y	z	$B_{eq}/Å^2$
O1	0.1304(1)	0.4152(2)	0.0982	4.2(1)
O2	0.4595(1)	-0.0192(2)	0.4275	4.9(1)
O3	0.3255(1)	0.0906(1)	-0.0469(2)	3.4(1)
O4	0.3494(1)	0.0339(2)	-0.2235	5.7(1)
O5	0.4450(1)	0.4361(2)	0.3963(3)	4.7(1)
O6	0.3495(1)	0.4153(2)	-0.4315(2)	4.4(1)
O7	0.2592(1)	0.6303(1)	0.0143(2)	3.22(9)
O8	0.1913(1)	0.7456(2)	0.0592(3)	5.4(1)
C1	0.3497(1)	0.1644(2)	0.0320(3)	3.0(1)
C2	0.2882(1)	0.2268(2)	0.0546(3)	2.9(1)
C3	0.2879(2)	0.2832(2)	0.1519(3)	3.6(1)
C4	0.2351(2)	0.3456(2)	0.1687(3)	3.5(1)
C5	0.1826(1)	0.3527(2)	0.0874(3)	3.1(1)
C6	0.1818(2)	0.2969(2)	-0.0094(4)	3.8(1)
C7	0.2343(2)	0.2350(2)	-0.0253(3)	3.5(1)
C8	0.3794(1)	0.1191(2)	0.1403(3)	2.7(1)
C9	0.3349(2)	0.0811(2)	0.2225(3)	3.7(2)
C10	0.3606(2)	0.0341(2)	0.3176(3)	3.9(2)
C11	0.4312(2)	0.0245(2)	0.3329(3)	3.4(1)
C12	0.4754(2)	0.0612(2)	0.2512(3)	3.9(2)
C13	0.4500(2)	0.1083(2)	0.1564(3)	3.4(1)
C14	0.4029(1)	0.2106(2)	-0.0436(3)	3.1(1)
C15	0.4432(2)	0.2868(2)	-0.0215(4)	4.2(2)
C16	0.4887(2)	0.3152(3)	-0.1065(5)	5.9(2)
C17	0.4935(3)	0.2698(4)	-0.2123(5)	6.9(3)
C18	0.4542(2)	0.1963(4)	-0.2368(4)	5.8(2)
C19	0.4088(2)	0.1669(2)	-0.1498(3)	3.7(1)
C20	0.3604(2)	0.0908(2)	-0.1487(3)	3.9(2)
C21	0.3339(1)	0.6109(2)	-0.0054(3)	2.7(1)
C22	0.3603(1)	0.5603(2)	0.1022(3)	2.6(1)
C23	0.4260(2)	0.5222(2)	0.1004(3)	3.2(1)
C24	0.4534(2)	0.4814(2)	0.1988(3)	3.6(1)
C25	0.4151(2)	0.4772(2)	0.3012(3)	3.2(1)
C26	0.3496(2)	0.5145(2)	0.3042(3)	3.6(2)
C27	0.3229(2)	0.5561(2)	0.2055(3)	3.3(1)
C28	0.3396(1)	0.5590(2)	-0.1191(3)	2.7(1)
C29	0.3254(2)	0.4664(2)	-0.1211(3)	3.1(1)
C30	0.3281(2)	0.4178(2)	-0.2231(3)	3.5(1)
C31	0.3449(2)	0.4604(2)	-0.3271(3)	3.0(1)
C32	0.3580(2)	0.5521(2)	-0.3280(3)	3.2(1)
C33	0.3550(2)	0.6005(2)	-0.2244(3)	2.9(1)
C34	0.3655(2)	0.7046(2)	-0.0070(3)	3.0(1)
C35	0.4331(2)	0.7309(2)	-0.0254(3)	3.6(1)
C36	0.4488(2)	0.8219(2)	-0.0136(4)	4.5(2)
C37	0.3977(2)	0.8838(2)	0.0158(4)	5.4(2)
C38	0.3301(2)	0.8584(2)	0.0322(4)	5.3(2)
C39	0.3147(2)	0.7667(2)	0.0202(3)	3.8(1)
C40	0.2486(2)	0.7185(2)	0.0342(3)	3.8(1)

$B\text{eq}=(4/3)\Sigma_i\Sigma_j\beta_{ij}a_i^*a_j^*(a_i a_j)$

Table 3 Selected bond lenghts (Å) and angles (°)

Atom	Atom	Distance	Atom	Atom	Distance
O1	C5	1.372(4)	O5	C25	1.369(4)
O2	C11	1.371(4)	O6	C31	1.368(4)
O3	C1	1.490(3)	O7	C21	1.484(3)
O3	C20	1.341(4)	O7	C40	1.343(3)
O4	C20	1.216(4)	O8	C40	1.208(4)
C1	C2	1.524(4)	C21	C22	1.524(4)
C1	C8	1.518(4)	C21	C28	1.511(4)
C1	C14	1.504(4)	C21	C34	1.517(4)
C19	C20	1.463(5)	C39	C40	1.469(5)

Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
C20	O3	C1	111.3(2)	C40	O7	C21	111.3(2)
O3	C1	C14	101.7(2)	O7	C21	C34	102.4(2)
O3	C1	C8	106.5(2)	O7	C21	C28	107.4(2)
O3	C1	C2	107.7(2)	O7	C21	C22	107.4(2)
C14	C1	C8	114.1(2)	C34	C21	C28	115.3(3)
C14	C1	C2	110.5(2)	C34	C21	C22	109.0(2)
C8	C1	C2	115.1(2)	C28	C21	C22	114.4(2)
O1	C5	C4	122.1(3)	O5	C25	C24	117.5(3)
O1	C5	C6	117.9(3)	O5	C25	C26	123.0(3)
O2	C11	C12	118.1(3)	O6	C31	C32	117.5(3)
O2	C11	C10	122.7(3)	O6	C31	C30	122.5(3)
C19	C14	C1	110.1(3)	C39	C34	C21	108.8(3)
C15	C14	C1	130.3(3)	C35	C34	C21	129.9(3)
C14	C19	C20	107.7(3)	C34	C39	C40	108.5(3)
C18	C19	C20	130.4(4)	C38	C39	C40	130.3(3)
O4	C20	O3	121.1(3)	O8	C40	O7	120.2(3)
O4	C20	C19	129.7(3)	O8	C40	C39	131.0(3)
O3	C20	C19	109.2(3)	O7	C40	C39	108.8(3)

Estimated standard deviations in the least significant figure are given in parentheses.

Figure Captions

Fig. 1 Dissociation equilibrium of phenolphthalein

Fig. 2 Molecular structure with the numbering of the atoms.
Thermal ellipsoids of the non-hydrogen atoms are scaled to enclose 50 % probability.
The spheres of the hydrogen atoms are drawn in an arbitrary scale.

Fig. 3 Molecular packing viewed along the *c* -axis.