Crystal Structure of Some Charge-Control Agents: 3,5-di-tert-butyl-2-hydroxybenzoic Acid and its Zinc Complexes

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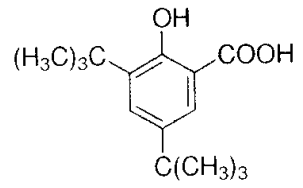
Abstract

The title compounds are charge-control agents used in electrophotography. In 3,5-Di-*tert*-butyl-2-hydroxybenzoic acid (TBS), there are two independent molecules A and B in the asymmetric unit. The molecules form centrosymmetric dimers A-A and B-B *via* pair of O–H···O hydrogen bonds between the two carboxyl groups. On the other hand, the zinc complex of TBS ($Zn(TBS)_2$) is found to include solvent molecules when recrystallized from ethanol and acetonitrile: $(Zn(TBS)_2)$ $(ethanol)_2$ and $(Zn(TBS)_2)$ $(acetnitrile)_2$. The former complex has C_2 symmetry, and exhibits a deformed octahedral coordination. Two O atoms of the ethanol molecules are coordinated in a *cis* fashion to the Zn atom. On the other hand, the latter forms a trinuclear complex: one central six-coordinate Zn complex and two four-coordinate Zn ones. Each O-ligand of TBS is coordinated to a different Zn atom.

1. Introduction

3,5-Di-*tert*-butyl-2-hydroxybenzoic acid (TBS; Fig.1(a)) is an industrially important, charge-control agent (CCA) of the negative type used in electrophotography, either embedded in toners or mixed with toners.[1]

(a)



(b)

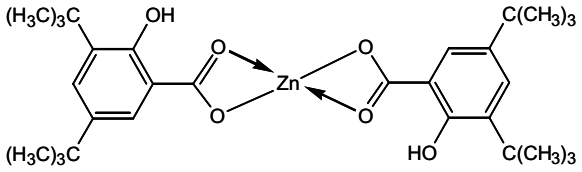


Figure 1. Molecular structure: (a) TBS and (b) E-84.

Furthermore, the charge-control power is greatly enhanced when TBS is combined with a variety of metals such as Zn, Cr, Al and Fe to yield metal complexes. Fig.1(b) shows an example of a 1:2 complex of the zinc salt (commonly known as E-84). However, it has been pointed out that the charge-control ability depends greatly on the process of toner preparation. So we assumed that the structural changes of the metal complexes or rearrangement of the molecules might occur during the toner preparation process. For this reason, we have carried out the structure analysis of TBS and its zinc complex as a preliminary step for the elucidation of the charge-control mechanism.

2. Experiment

2-1 Materials and Their Crystal Growth

TBS was obtained from API Corporation. Single crystals were grown by recrystallization from an ethanol solution. A number of transparent, colorless crystals were obtained in block forms.

E-84 was obtained from Orient Chemical Industries, Ltd. Single crystals were grown from solution in ethanol and acetonitrile. Transparent, single crystals were obtained in the form of needles from an ethanol solution; whereas crystals of the tetragonal form were isolated when recrystallized from an acetonitrile solution. These single crystals were found to include solvent molecules according to the thermogravi-metiric analysis (TGA).

2-2 Data Collection and Structure Analysis

The reflection data of TBS and E-84 were collected by a Rigaku Diffractometer (model: Rapid F).[2] Both experiments were carried out at 93 K, since the solvent molecules are rapidly lost at room temperature. The structure was solved by direct methods using a program of SHELXS86.[3] Refinement was then made on F^2 by full-matrix least-squares calculations using the teXsan program package.[4]

In TBS, the H atoms of the carboxyl and hydroxyl groups were found in different density maps and their coordinates were refined, with $U_{iso} = 0.0541$ Å^2. All other H atoms were positioned by calculation and not refined [C–H = 0.95 Å and $U_{iso} = 1.2\ U_{eq}$].

On the other hand, in E-84/(ethanol)$_2$, the ethanol molecule was disordered; the minimum *R* value was obtained with an occupancy of 0.5(1) for atoms C16, C17, C18 and C19. The well-modelled pairs are O4/C16/C17 and O4/C18/C19. The H atom of the hydroxyl group of the TBS ligand was found in a difference density map but not refined. The hydroxyl H atom of the ethanol molecule could not be located in the difference density map and therefore this H atom remained undetermined. All other H atoms were positioned by calculation and allowed for as riding.

The single crystals recrystallized from solution in acetonitrile is found to form a trinuclear complex: one central six-coordinate Zn complex and two four-coordinate Zn ones.

3. Results and Discussion

3-1 Crystallographic Parameters of TBS and E-84/(Ethanol)$_2$

Table 1 details the crystallographic parameters for TBS[4] and E-84/(ethanol)$_2$.[5]

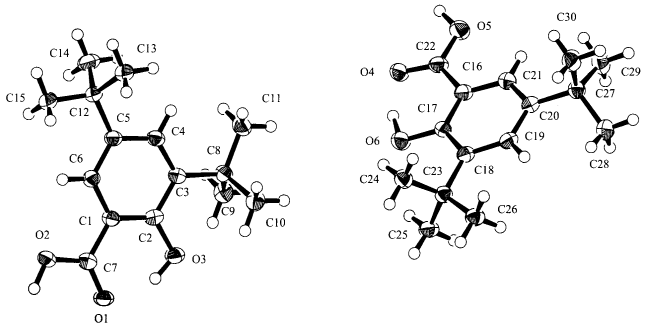


Figure 2. Two independent molecules (left: A, right: B) of TBS, showing 50% displacement ellipsoids for non-H atoms.

Table 1. Crystallographic Parameters for TBS, E-84 and E-84(Acetonitrile)$_2$.

	TBS[5)]	E-84[6)]	E-84(acetonitrile)$_2$
Molecular formula	$C_{15}H_{22}O_3$	$Zn(C_{15}H_{21}O_3)_2(C_2H_6O)_2$	$C_{94}H_{132}N_2O_{18}Zn_3$
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P*-1	*C*2/*c*	$P2_1/c$
Z	4	4	2
Molecular weight	250.34	656.18	1774.22
Molecular symmetry	C_1	C_2	C_i
a (Å)	9.597(2)	33.891(4)	17.518(3)
b (Å)	9.828(2)	11.191(1)	16.667(3)
c (Å)	17.783(3)	9.491(1)	18.414(3)
α(°)	74.16(1)	-	-
β(°)	78.85(1)	86.97(1)	113.25(1)
γ(°)	65.11(1)	-	-
R	0.037	0.042	0.082

3-2 TBS

There are two independent molecules A and B as shown in Fig.2 and their bond parameters are given in Table 2. These molecules occupy the general position to give 4 molecules per unit cell. The conformation of both molecules is quite similar, and there exits an intramolecular hydrogen bond between the phenol OH and the O atom of the carboxylic acid (Table 3). The molecules are dimerized in the crystal structure, as shown in Fig. 3, by O–H···O intermolecular hydrogen bonds between the two carboxyl groups. There are two types of centrosymmetric dimers, A-A and B-B, in the unit cell. Although the present hydrogen-bond formation is typical of the carboxylic acid, there is a small step of *ca* 0.89 Å between the two hydrogen-bonded molecular planes for A-A and B-B dimers (Fig. 4).

Table 2. Selected Geometric Parameters (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O1	0.93 (2)	1.76 (2)	2.613 (2)	151 (2)
O6—H7···O4	1.07 (2)	1.56 (2)	2.579 (2)	158 (2)
O2—H4···O1^{i}	0.97 (2)	1.69 (2)	2.659 (2)	177 (2)
O5—H8···O4^{ii}	0.92 (2)	1.74 (2)	2.661 (2)	179 (2)

Symmetry codes: (i) $1-x, -y, -z$; (ii) $-x, 2-y, 1-z$.

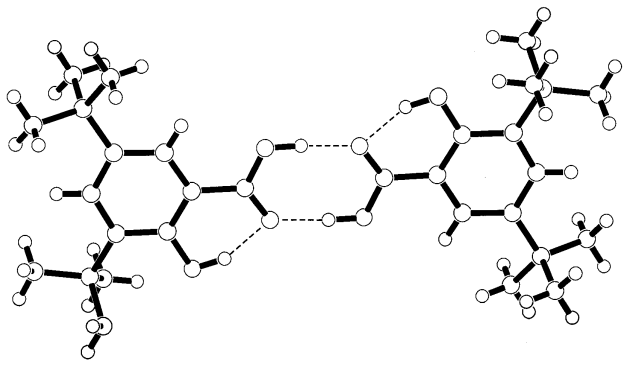


Figure 3. Top view of the hydrogen-bonded dimer A-A.

Table 3. Hydrogen-Bonding Geometry (Å, °).

O1—C7	1.243 (2)	C1—C7	1.464 (3)
O2—C7	1.324 (2)	C3—C8	1.541 (3)
O3—C2	1.353 (2)	C5—C12	1.535 (3)
O4—C22	1.248 (2)	C16—C22	1.466 (3)
O5—C22	1.325 (2)	C18—C23	1.547 (3)
O6—C17	1.364 (2)	C20—C27	1.538 (3)
O1—C7—O2	120.4 (2)	O4—C22—O5	121.2 (2)
O1—C7—C1	123.7 (2)	O4—C22—C16	122.9 (2)
O2—C7—C1	115.9 (2)	O5—C22—C16	115.9 (2)

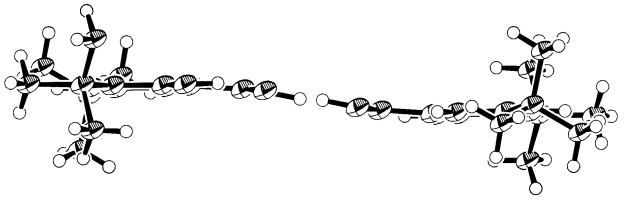


Figure 4. Side view of the hydrogen-bonded dimer A-A.

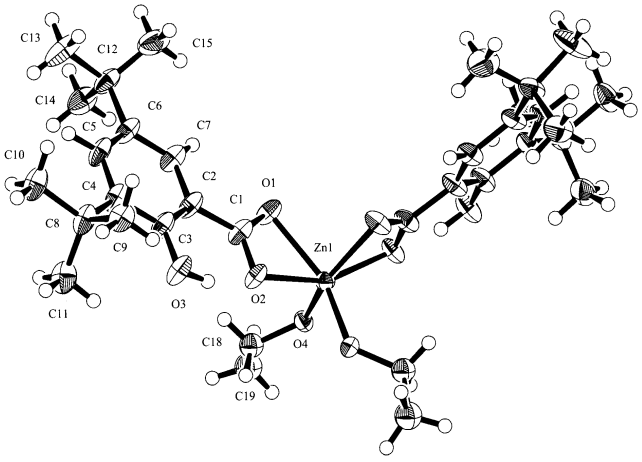


Figure 5. A view of the molecular structure of E-84/(ethanol)$_2$, showing 50% displacement ellipsoids for non-H atoms. The occupation factors of the ethanol atoms C18 and C19 are 50%, and the other possible orientations of the ethanol molecules have been omitted. The H atom bonded to atom O4 was not located.

3-3 E-84/(Ethanol)$_2$

Figure 5 shows the ORTEP plot of E-84/(ethanol)$_2$ which has C_2 symmetry. Two O atoms of the ethanol molecules are coordinated in a *cis* fashion to the Zn atom to form a deformed octahedral complex (Table 4). The chelate rings formed by the TBS ligands are almost perpendicular to each other. There is an intramolecular hydrogen bond between the OH group and the carbonyl O atom in the TBS ligand. The molecules pack as shown in Fig. 6. The short O1···O4 (1-x, 2-y, 1-z) distance of 2.625(2) Å suggests an intermolecular hydrogen bond.

Table 4. Selected Geometric Parameters (Å, °).

Zn1—O1	2.237 (2)	O3—C3	1.348 (4)
Zn1—O2	2.070 (2)	O4—C16	1.469 (6)
Zn1—O4	2.034 (2)	O4—C18	1.458 (6)
O1—C1	1.264 (3)	C16—C17	1.503 (8)
O2—C1	1.280 (3)	C18—C19	1.507 (9)
O1—Zn1—O1^{i}	87.9 (1)	O4—Zn1—O4^{i}	97.7 (1)
O1—Zn1—O2	60.86 (7)	Zn1—O1—C1	86.7 (2)
O1—Zn1—O2^{i}	100.27 (8)	Zn1—O2—C1	93.9 (2)
O1—Zn1—O4	94.01 (7)	Zn1—O4—C16	119.2 (3)
O1—Zn1—O4^{i}	151.28 (7)	Zn1—O4—C18	126.7 (3)
O2—Zn1—O2^{i}	155.2 (1)	O4—C16—C17	110.0 (5)
O2—Zn1—O4	105.68 (7)	O4—C18—C19	111.9 (5)
O2—Zn1—O4^{i}	90.67 (7)		

Symmetry code: (i) $-x, y, \frac{1}{2}-z$.

Table 5. Hydrogen-Bonding Geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1···O2	0.91	1.72	2.573 (3)	156

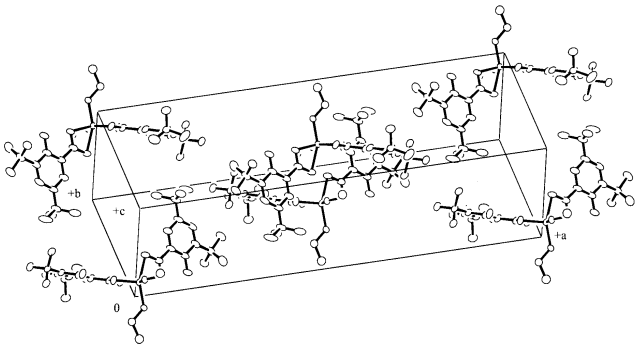


Figure 6. The crystal structure of E-84/(ethanol)$_2$. One of two possible orientations of the disordered ethanol molecules has been omitted for clarity.

3-4 E-84/(Acetonitrile)$_2$

Figure 7 shows the conformation of the trinuclear complex composed of E-84 and acetonitrile molecules: $Zn_3(TBS)_6(acetonitrile)_2$. There are three Zn atoms which form one central six-coordinate complex and four-coordinate Zn ones. It is of interest to note that all TBSs are coordinated to Zn atoms as bidentate, but each O-atom (*i.e.* ligand) of TBS is bonded to a different Zn-atom. The four-coordinate Zn complex located above and below the central six-coordinate Zn-atom accommodates one N-atom of acetonitrile.

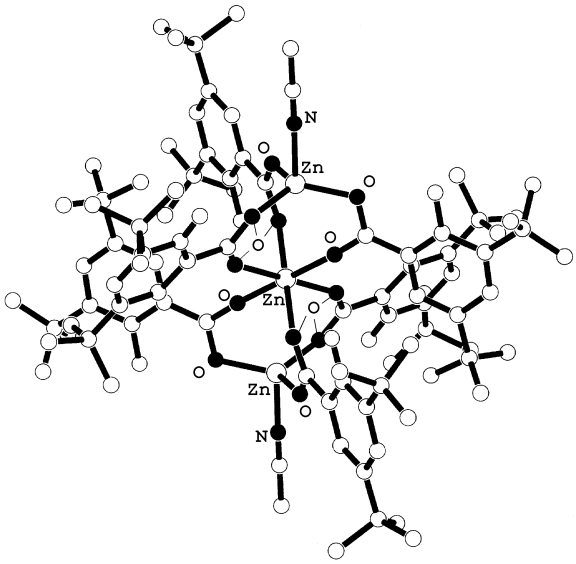


Figure 7. Molecular conformation of acetonitrile-solvated E-84.

Conclusions

1. There are two sorts of intermolecularly hydrogen bonded dimers (AA & BB) in TBS. The H-bonded molecules lie not entirely on the molecular plane, but there is a step of *ca* 0.89 Å around the bridging H-bond.
2. E-84 is found to easily include solvent molecules when recrystallized from solution in ethanol and acetonitrile.
3. In E-84/(ethanol)$_2$, TBS molecules are coordinated as bidentate to the central Zn atom through the O-atoms. The coordination number is six.
4. Acetonitrile-solvated E-84 forms a trinuclear complex composed of one six-coordinate Zn complex and two four-coordinate Zn ones. TBSs are coordinated to Zn atoms as bidentate, but each O-atom (*i.e.* ligand) of TBS is bonded to a different Zn-atom.

References

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Biography

Jin Mizuguchi obtained his B. Sc. in chemistry from Sophia University in 1970, Dr. of Sc. from the University of Tokyo in 1982 and Venia Docendi ("Habilitation") from the University of Bern in 1994. He worked at Sony Corporation Research Center from 1970 to 1985 and at Ciba-Geigy AG (Switzerland) from 1985 to 1995. Since 1995, Prof. Mizuguchi has been at Yokohama National University as professor of materials science. His current interest is centered on the electronic characterization of organic pigments and their applications.