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1,6-Dioxa [6.5] orthocyclophane-13, 16-diene-15-one[DOCD] crystallizes in triclinic $P\bar{1}$ space group and the relevant crystal data are: $a=7.577(3)$ Å, $b=10.425(5)$ Å, $c=10.935(5)$ Å, $\alpha=87.89(1)^\circ$, $\beta=78.13(1)^\circ$, $\gamma=78.87(1)^\circ$, $V=829.4(6)$ Å^3, $Z=2$, $D_{cal}=1.283\,Mg/m^3$. The structure was solved by direct methods and refined by least-squares procedures to a final R-value of 0.0466. The structure is 15-mer whose maximum internal cavity diameter was found to be 6.44 Å. The butyl group adopts a zigzag conformation. The crystal structure is stabilized by C– . . . O types of hydrogen bondings and C–H. . .π weak interactions in addition to van der Waals forces.

Keywords: conformation; cyclophane; DOCD; hydrogen bondings; macrocyclic

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INTRODUCTION

Macrocyclic ligands are closed-system compounds containing a minimum of nine atoms with at least three donor atoms [1] such as oxygen, nitrogen, sulphur, phosphorus, and arsenic. These types of macrocycles tend to have considerable affinity for transition and other heavy metals. Christensen and coworkers [2] have discussed several classes of macrocycles and their unique ion-binding properties with different applications. The chemistry of oxygen-containing macrocycles and the structures of various complexes are discussed by Izatt and his coworkers [3].

Macrocyclic ligands are used as models for protein–metal binding sites in a substantial array of metalloproteins in biological systems, as synthetic ionophores, as models to study the magnetic exchange phenomena, as therapeutic reagents in chelate therapy for the treatment of metal intoxication, as cyclic antibiotics to perform action to specific metal complexation to study the guest–host interactions, and in catalysis [4]. Also, ligands are used for diverse processes such as separation of ions by transport through artificial and natural membranes, liquid–liquid or solid–solid phase transfer reactions, and dissolution in apolar solvents of metal and organic salts.

The significance of this supramolecular chemistry has been extended to varied applications, in particular enzyme mimics [5] and conduction of molecules [6]. It differs from the conventional ones in the noncovalent nature of its bonds, which form the basis for information transfer between molecules in living systems. Elucidation of these noncovalent interactions between the host and guest molecules may bring new approaches in pharmacy, medicine, and chemistry [7]. The supramolecules can recognize a specific molecule, capture it by means of electrostatic bonds or by a combination of hydrophobic interactions, and then trap the specified molecule, atom, or ion.

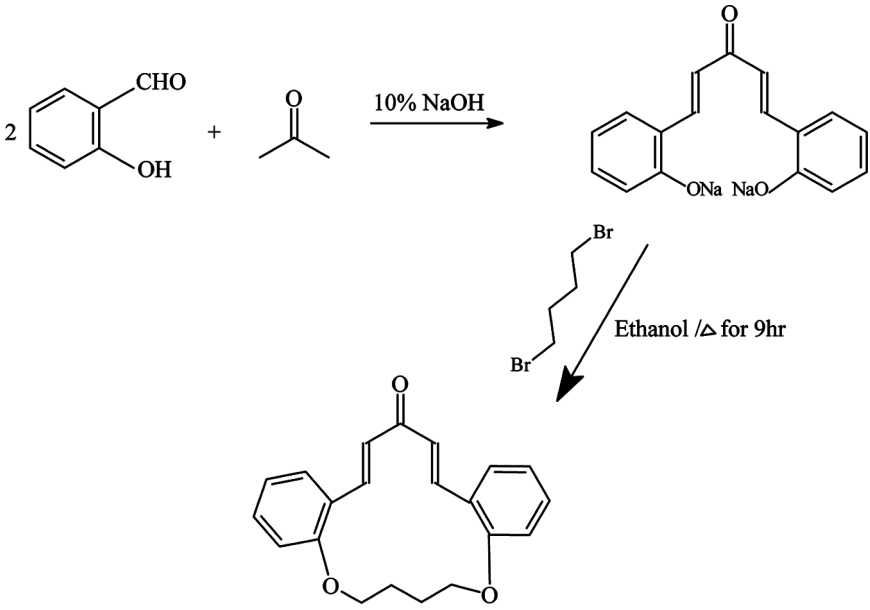
Among the supramolecules, cyclophanes are the class of compounds that have a macrocyclic framework with either hydrophilic or hydrophobic rigid cavity. Hence, there is a need to synthesize and characterize the macrocyclic ring molecules with required geometry, configuration, and cavity size. The aromatic structural units present in the cyclophanes ensure the rigidity of the molecular structure and thereby impose the reorganization of aromatic moieties for cooperative binding of the guests.

X-RAY DATA COLLECTION

Intensity data were collected on Siemens SMART CCD [8] area detector diffractometer using graphite monochromated MoK_{α}

TABLE 1 Crystal Data

Parameters	DOCD
CCDC No.	CCDC 254253
Empirical formula	$C_{21}H_{20}O_3$
Formula weight	320.37
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	$a = 7.577(3)$ Å; $\alpha = 87.89(1)^\circ$ $b = 10.425(5)$ Å; $\beta = 78.13(1)^\circ$ $c = 10.935(5)$ Å; $\gamma = 78.87(1)^\circ$
Volume	829.4(6) Å^3
Z, calculated density	2, 1.283 Mg/m^3
$F(000)$	340
Limiting indices	$-9 \le h \le 9$ $-12 \le k \le 13$ $-13 \le l \le 13$
Reflections collected/unique/$I > 2\sigma(I)$	8252/3226/2592
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3226/0/298
Goodness-of-fit on F^2	1.053
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0466$, w$R_2 = 0.1220$
Largest diff. peak and hole	0.216 and -0.172 e.Å^{-3}



SCHEME 1 Synthetic route for DOCD.

radiation ($\lambda = 0.71073$ Å) at 293(2) K. The whole data collection was covered over a hemisphere of reciprocal space by a combination of three sets of exposure, each having a different Φ angle (0, 88, and 180°) for the crystal, and each exposure time of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm, and the detector swing angle was −35°. Coverage of the unique set was complete by more than 91.5%. Out of 8252 reflections collected for the whole sphere, 3226 observed reflections were used for structure solution and refinement. The intensity data were corrected for Lorentz and polarization effects.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods implemented in program SHELXS97 [9] and refined on F^2 by full-matrix least-squares

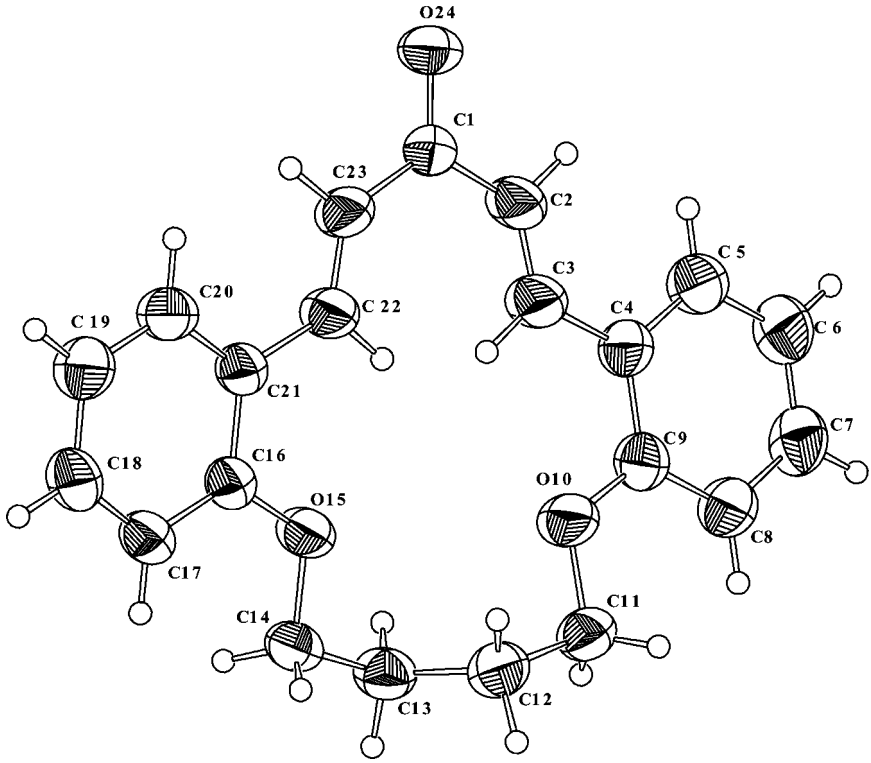
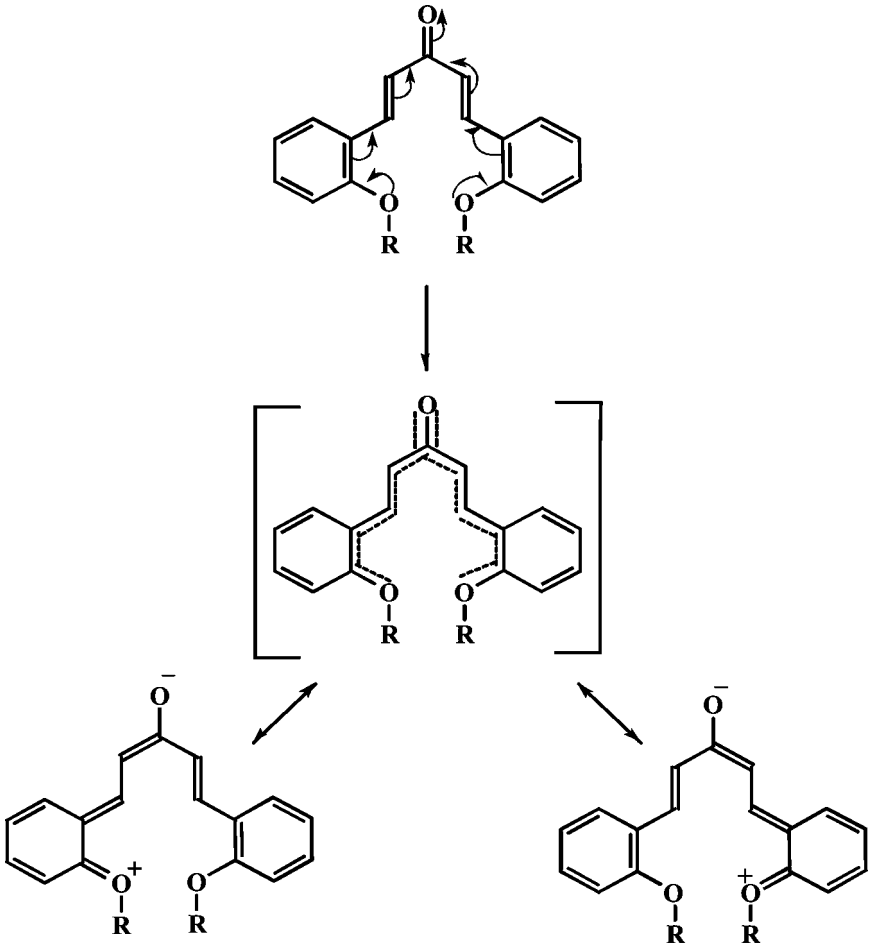


FIGURE 1 ZORTEP plot of the molecule showing 50% probability thermal displacement ellipsoids with H atoms.

procedures using the program SHELXL97 [9]. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were located by computing a difference Fourier map. The final cycle of refinement converged to $R_1 = 0.0466$ and $wR_2 = 0.1218$ for the observed reflections. The maximum and minimum heights in the final difference Fourier map were 0.216 and $-0.172\,e.\mathring{A}^{-3}$, respectively. The geometrical calculations were done using the program PARST [10], and figures were drawn using ZORTEP [11] and



R= -CH_2-CH_2-CH_2-CH_2-

SCHEME 2 Resonance structures for DOCD.

PLATON [12]. The crystal data and other relevant parameters are given in Table 1.

RESULTS AND DISCUSSION

As a part of our ongoing study on large-ring molecules, we are in the process of developing large cyclic ethers (Scheme 1). The perspective view of the molecule is shown in Fig. 1. The internal cavity size of the molecule (C1 . . . C13) is 6.44 Å. The 1,4-dioxy butane group through O10-C11-C12-C13-C14-O15 atoms possesses a zigzag conformation as can be seen from the torsion angles [(C9-O10-C11-C12 =) 173.8(2)°; (O10-C11-C12-C13) = 71.4(2)°; (C11-C12-C13-C14 =) −147.6(2)°; (C12-C13-C14-O15 =) 68.9(2)°; (C13-C14-C15-C16 =) 176.6(1)°].

This cyclophane contains two planar phenyl rings (C4 through C9 and C16 through C21), oriented synclinally with each other at an

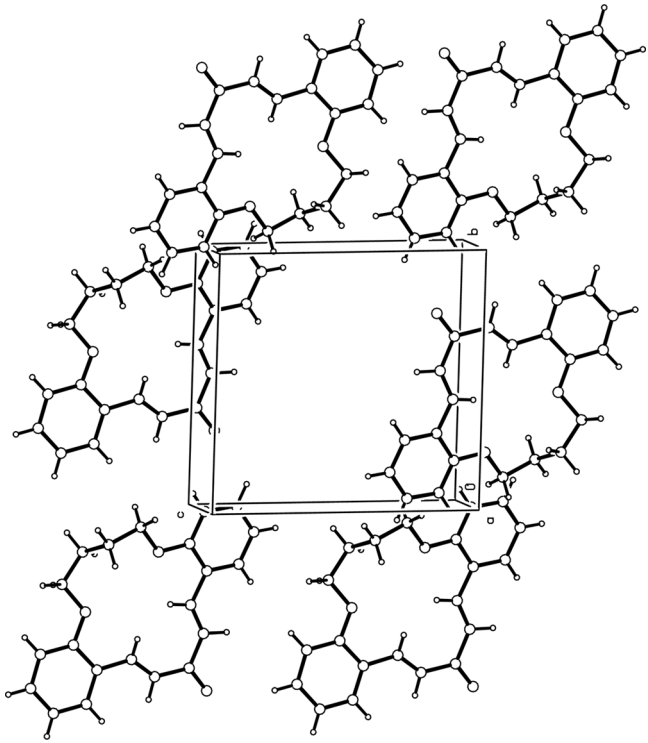


FIGURE 2 Packing of the molecules viewed down the *a*-axis.

TABLE 2 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)

Atoms	*x*	*y*	*z*	U_{eq}^a
C1	2481(2)	6398(2)	10422(1)	47(1)
C2	2359(3)	6709(2)	9124(2)	60(1)
C3	2265(3)	6022(2)	8227(2)	68(1)
C4	2165(2)	6403(2)	6936(2)	53(1)
C5	1903(3)	7702(2)	6551(2)	62(1)
C6	1861(3)	8032(2)	5322(2)	65(1)
C7	2080(3)	7070(2)	4457(2)	62(1)
C8	2322(3)	5770(2)	4807(2)	59(1)
C9	2356(2)	5434(2)	6041(2)	53(1)
O10	2587(2)	4186(1)	6475(1)	67(1)
C11	3061(3)	3124(2)	5611(2)	56(1)
C12	3417(3)	1910(2)	6379(2)	57(1)
C13	1689(3)	1575(2)	7197(29)	55(1)
C14	1985(3)	930(2)	8410(2)	54(1)
O15	2373(2)	1909(1)	9139(10	58(1)
C16	2608(2)	1627(1)	10322(1)	45(1)
C17	2665(2)	395(2)	10854(2)	51(1)
C18	2894(3)	209(2)	12066(2)	58(1)
C19	3079(3)	1228(2)	12758(2)	65(1)
C20	3029(3)	2455(2)	12225(2)	58(1)
C21	2781(2)	2683(1)	11012(1)	46(1)
C22	2694(3)	3981(2)	10433(2)	58(1)
C23	2554(3)	5077(2)	10931(2)	64(1)
O24	2535(2)	7285(1)	11112(1)	67(1)

$^a U_{eq} = (1/3) \sum_i \sum_j a_i^* a_j^* a_i \cdot a_j$.

TABLE 3 Hydrogen-Bonding Geometry (Å, °)

D-H...A	D-H	D...A	H...A	D-H...A
C22-H17...O15	0.863(4)	2.701(2)	2.278(4)	113
C3-H18...O10	0.930(4)	2.700(2)	2.319(4)	107
C13-H3...O24^{i}	0.986(2)	3.367(2)	2.655(2)	130
C17-H13...O24^{ii}	0.949(2)	3.262(3)	2.589(2)	129
C18-H9...O24^{ii}	0.915(2)	3.336(3)	2.771(2)	124
C7-H15...O24^{iii}	0.936(2)	3.606(3)	2.690(2)	168
C11-H4... Cg1^{iv}	0.970	3.668	2.799	151
C14-H10... Cg2^{v}	0.970	4.217	3.294	155

Notes: Equivalent positions: (i) $-x, 1-y, 2-z$; (ii) $x, y-1, z$; (iii) $x, y, z-1$; (iv) $1-x, 1-y, 1-z$; (v) $1-x, 2-y, -z$.

Cg1 = C4 through C9; Cg2 = C16 through C21.

Cg is the centroid of the benzene ring.

angle of 12.4(3)°. A study of torsion angles, least-squares planes, and asymmetry parameters [$Q_T = 0.19(2)$ Å] suggests that the whole molecule is almost planar except the butyl group, which is in zigzag conformation. An in-depth analysis of bond lengths and torsion angles reveals that the 15-mer ring suffers the delocalization effect, and the alternative form is shown in Scheme 2.

In this structure, three short contacts of H...H are observed [H2...H5 = 2.19(4) Å, H20... H23 = 2.20(2) Å, and H3...H22 = 2.0(1) Å]. The distance between H3 and H22 atoms is comparatively shortened; in turn electron–electron repulsion between the atoms is expected. This causes the deviation of the benzene rings from the coplanarity to synclinal configuration in the structure.

The packing of the molecules in the unit cell viewed down the c-axis is shown in Fig. 2. The C–H ... O types of intra- and intermolecular hydrogen bondings play a major role in crystal packing. The weak C–H...π interactions [13] are also useful in stabilizing the molecules in the unit cell in addition to van der Waals forces. The details of hydrogen bonding networks are given in Table 3.

EXPERIMENTAL

Disodium disalicylidine acetone (4.36 g, 0.01 mol) was suspended in ethanol (50 mL), and 1, 4-dibromobutane (2.16 g, 0.01 mol) was added. The mixture was refluxed for 9 h. The solution was poured into ice water (200 mL), and the precipitate was filtered and recrystallized from ethyl acetate to yield the compound (1.86 g, 58%). The suitable crystals for X-ray crystallographic study were obtained from ethanol by the slow evaporation method. The compound preparation is shown in Scheme 1.

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