

Benzo-15-Crown-5 1:1 and 1:2 Complexes with Dithiooxamide and Thioacetamide

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Abstract. Benzo-15-crown-5 and thiooxamide in the 1:1 complex form infinite chains of alternating host-guest molecules. The host oxygen atoms are involved in six close interactions with amide hydrogen atoms forming one bifurcated and one single hydrogen interaction on each face. In the 1:2 complex the host forms a distinct molecular entity with two thioacetamide molecules. Again one bifurcated and one normal hydrogen···oxygen interaction occurs on each face. The conformation of the benzo-15-crown-5 host is the same in both complexes and agrees with a conformation of the free host calculated by molecular mechanics. The conformation of crystalline benzo-15-crown-5 differs from that calculated. In either case, no major conformational reorganization is required to accommodate the intermolecular interactions. The oxygen atoms of the benzo-15-crown-5 form an approximate pentagon with the amide nitrogen atoms lying 2.18(1) Å from the mean plane.

Key words: Benzo-15-crown-5, dithiooxamide, thioacetamide, hydrogen bonding, X-ray diffraction, molecular mechanics.

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1. Introduction

The study of well-defined complexes formed between uncharged molecules is of considerable interest because such interactions play fundamental roles in many biochemical processes [1]. The importance of such interactions in normal chemical reactions also may be an area which is not fully appreciated or exploited. The changes in host conformation accompanying weak but specific interactions with guest molecules is of particular interest [2]. In some cases conformational change may arise primarily from a reduction of intramolecular dipolar interactions rather than the formation of strong intermolecular hydrogen-like bonds [3]. This is particularly true for many complexes involving the spatial fitting of acidic $-\text{CH}_3$ and $-\text{CH}_2-$ groups. As part of a program to investigate spatial relationships, host conformational requirements and dynamics of conformational change, we report the structures of two complexes of benzo-15-crown-5.

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Table I. Crystal and molecular data for complexes **1** and **2**

1	2
$C_{14}H_{20}O_5 \cdot C_2S_2N_2H_4$	$C_{14}H_{20}O_5 \cdot 2C_2H_5NS$
$MW = 388.51$	$MW = 418.54$
$P\bar{1}$	Pc
$a = 9.314(2), b = 15.692(4)$	$a = 9.021(4), b = 15.352(6)$
$c = 8.040(1) \text{ \AA}, \alpha = 89.77(2)$	$c = 9.285(5) \text{ \AA}, \beta = 118.46(3)^\circ$
$\beta = 104.81(1), \gamma = 121.16(1)^\circ$	—
$V = 959.8(3) \text{ \AA}^3$	$V = 1130.5(9) \text{ \AA}^3$
$Z = 2, \mu = 27.11 \text{ cm}^{-1}$	$Z = 2, \mu = 23.40 \text{ cm}^{-1}$
$d_x = 1.33, d_c = 1.344 \text{ g cm}^{-3}$	$d_x = 1.21, d_c = 1.229 \text{ g cm}^{-3}$
2576 reflections	1649 reflections
$2102 \geq 2\sigma(I)$	$1629 \geq 2\sigma(I)$
$R = 0.035, R_w = 0.039$	$R = 0.033, R_w = 0.039$

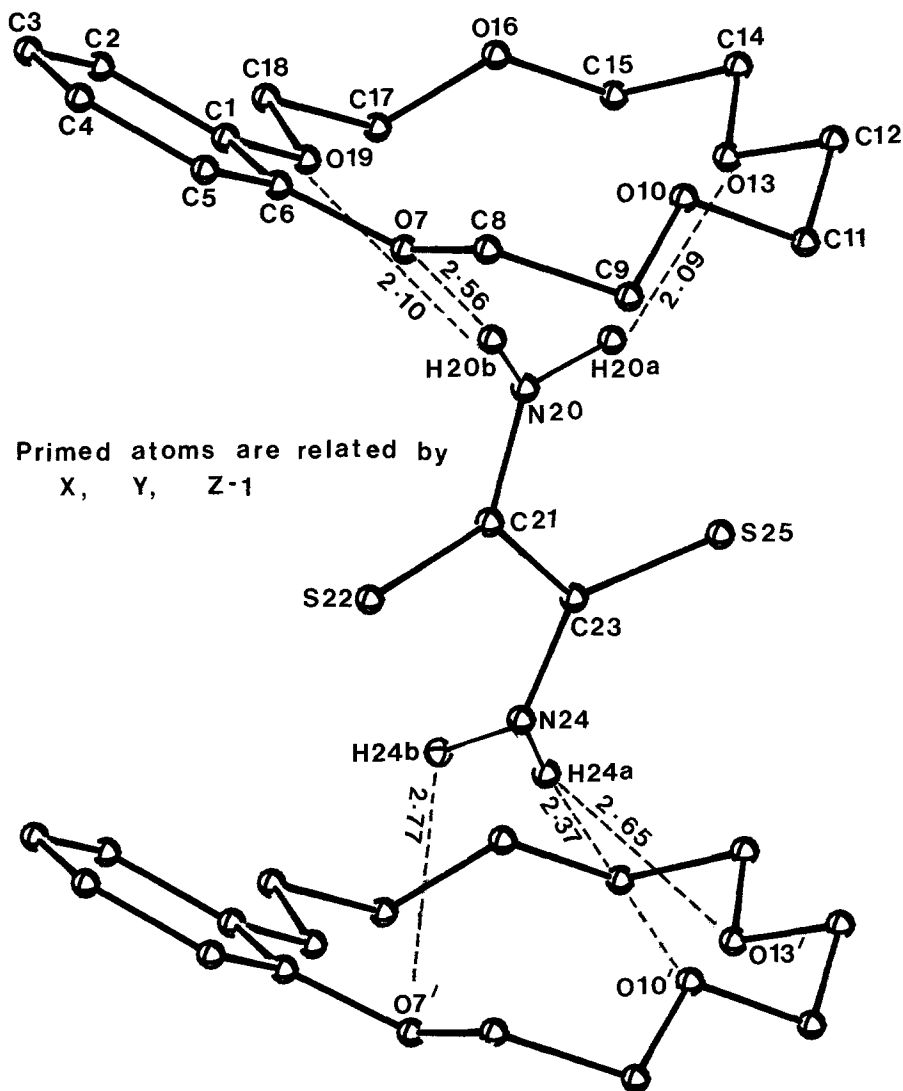


Fig. 1. Ortep drawing of the 1:1 complex between benzo-15-crown-5 and dithiooxamide.

2. Experimental

Compound 1. A 1 : 1 molar ratio of benzo-15-crown-5 (1.75 mmol) and dithiooxamide (1.75 mmol) was refluxed in a minimum quantity of ethylacetate. The hot solution was filtered, the flask cooled in an ice bath, and an almost quantitative yield of orange crystals was recovered by filtration. The 1 : 1 complex was recrystallized from ethylacetate yielding well-formed crystals (m.p. = 161.5–162.5 °C) suitable for X-ray analysis. A crystal was ground into an approximate sphere with a diameter of 0.23 to 0.25 mm. Crystal and molecular data are given in Table I and atomic positional parameters in Table II. Figure 1 is an Ortep drawing showing H···O interactions.

Table II. Atomic positional parameters ($\times 10^4$) and U_{eq}^a values ($\times 10^3$) for compound **1**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(1)	3433(3)	1908(2)	3183(3)	48(2)
C(2)	4796(4)	1874(2)	4260(4)	60(2)
C(3)	4449(5)	991(3)	4960(4)	70(3)
C(4)	2758(5)	155(3)	4483(4)	69(3)
C(5)	1388(4)	181(2)	3398(3)	57(2)
C(6)	1727(3)	1063(2)	2694(3)	44(2)
O(7)	475(2)	1180(1)	1610(2)	45(1)
C(8)	−1342(3)	374(2)	1232(4)	56(2)
C(9)	−2432(3)	726(2)	150(4)	56(2)
O(10)	−2273(2)	1521(2)	1154(2)	60(1)
C(11)	−3004(4)	2028(3)	162(4)	69(2)
C(12)	−2064(4)	3089(2)	1115(4)	64(2)
O(13)	−285(2)	3563(1)	1104(2)	60(1)
C(14)	833(4)	4564(2)	2022(4)	59(2)
C(15)	2618(4)	4931(3)	1872(4)	60(2)
O(16)	3249(2)	4376(1)	2852(2)	55(1)
C(17)	4758(4)	4496(2)	2569(4)	68(2)
C(18)	5070(4)	3709(2)	3396(4)	61(2)
O(19)	3620(2)	2751(1)	2469(2)	48(1)
N(20)	1261(3)	2769(2)	−822(2)	48(1)
C(21)	1715(3)	2681(2)	−2232(3)	41(1)
S(22)	3118(1)	2362(1)	−2297(1)	56(1)
C(23)	754(3)	2906(2)	−3821(3)	43(1)
N(24)	862(3)	2606(2)	−5291(3)	56(2)
S(25)	−244(1)	3513(1)	−3672(1)	77(1)

$$^a U_{eq} = 1/3[U_{11}(a \cdot a^*)^2 + U_{22}(b \cdot b^*)^2 + U_{33}(c \cdot c^*)^2 + 2U_{12}aba^*c^* \cos \gamma + 2U_{13}aca^*c^* \cos \alpha + 2U_{23}bcb^*c^* \cos \beta].$$

Compound 2. A 1 : 2 molar ratio of benzo-15-crown-5 (2.5 mmol) and thioacetamide (5.0 mmol) was refluxed in a minimum quantity of ethylacetate. Treatment as described for compound **1** provided an almost quantitative yield of off-white crystals, m.p. 85–86 °C. A crystal was ground into an approximate sphere with a diameter of 0.22 to 0.25 mm. Crystal and molecular data are given in Table I and atomic positional parameters in Table III. Figure 2 is an Ortep drawing showing H···O interactions.

All intensity data were collected on a Syntex P2₁ diffractometer system using a θ : 2θ scan, $6.7 \leq 2\theta \leq 120^\circ$, a variable scan rate, and graphite monochromated $\text{CuK}\alpha$ radiation. Lattice

parameters were obtained by a least-squares refinement of 15 reflections whose angles were measured by a centering routine associated with the diffractometer system. Space groups were consistent with statistics and systematic absences. Monitored reflections showed no significant changes in intensity and carefully collected equivalent reflections yielded $R_{\text{int}} = 0.012$ and 0.017 for **1** and **2**, respectively. Consideration of crystal shape and of R_{int} led to neglect of absorption. The structures were solved by the application of direct methods [4]. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o)$ was obtained from counting

Table III. Atomic positional parameters ($\times 10^4$) and U_{eq}^a values ($\times 10^3$) for compound **2**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C(1)	1157(0)	2708(2)	3991(0)	42(2)
C(2)	615(5)	2821(3)	5136(5)	54(3)
C(3)	-392(6)	3566(4)	5002(7)	70(3)
C(4)	-809(5)	4145(3)	3762(6)	54(3)
C(5)	-253(5)	4035(3)	2660(6)	62(2)
C(6)	735(5)	3332(2)	2727(5)	47(2)
O(7)	1313(4)	3141(2)	1652(3)	49(1)
C(8)	1219(5)	3814(3)	535(5)	53(2)
C(9)	2036(6)	3438(3)	-418(5)	61(2)
O(10)	3738(4)	3222(2)	688(3)	57(2)
C(11)	4550(7)	2734(3)	-97(6)	80(3)
C(12)	6084(7)	2308(3)	1182(6)	73(3)
O(13)	5569(4)	1645(2)	1898(4)	66(2)
C(14)	6883(6)	1283(3)	3359(6)	77(3)
C(15)	6108(6)	745(3)	4151(6)	65(2)
O(16)	5171(4)	1325(2)	4641(4)	59(2)
C(17)	4092(6)	896(3)	5108(6)	65(3)
C(18)	3117(6)	1560(3)	5470(5)	61(3)
O(19)	2055(3)	2008(1)	3928(3)	44(1)
C(20)	604(5)	1089(2)	-548(5)	42(2)
C(21)	-1041(6)	1233(3)	-560(6)	72(3)
S(22)	609(2)	724(1)	-2208(2)	73(1)
N(23)	1963(4)	1287(2)	798(4)	53(2)
C(24)	5633(5)	3808(2)	5448(4)	41(2)
C(25)	5176(8)	4702(3)	4818(6)	90(3)
N(26)	5207(4)	3204(2)	4338(4)	50(2)
S(27)	6616(2)	3599(1)	7451(2)	65(1)

$$^a U_{\text{eq}} = 1/3[U_{11}(a \cdot a8)^2 + U_{22}(b \cdot b8)^2 + U_{33}(c \cdot c^*)^2 + 2U_{12}aba^*b^* \cos \gamma + 2U_{13}aca^*c^* \cos \alpha + 2U_{23}beb^*c^* \cos \beta].$$

statistics. Atomic scattering factors for C, N, O and S are those of Cromer and Mann [5] while those for H were obtained from Stewart *et al.* [6]. Sulfur was corrected for the real component of the anomalous dispersion. Table IV gives bond lengths and valence angles for **1** and **2** while Table V gives torsion angles around the 15-crown-5 moiety for **1**, **2**, a corresponding calculated conformer **A**, crystalline benzo-15-crown-5 [7] **3** and the corresponding calculated conformer **B**. Table VI lists all potential hydrogen...oxygen interactions in compounds **1** and **2**.

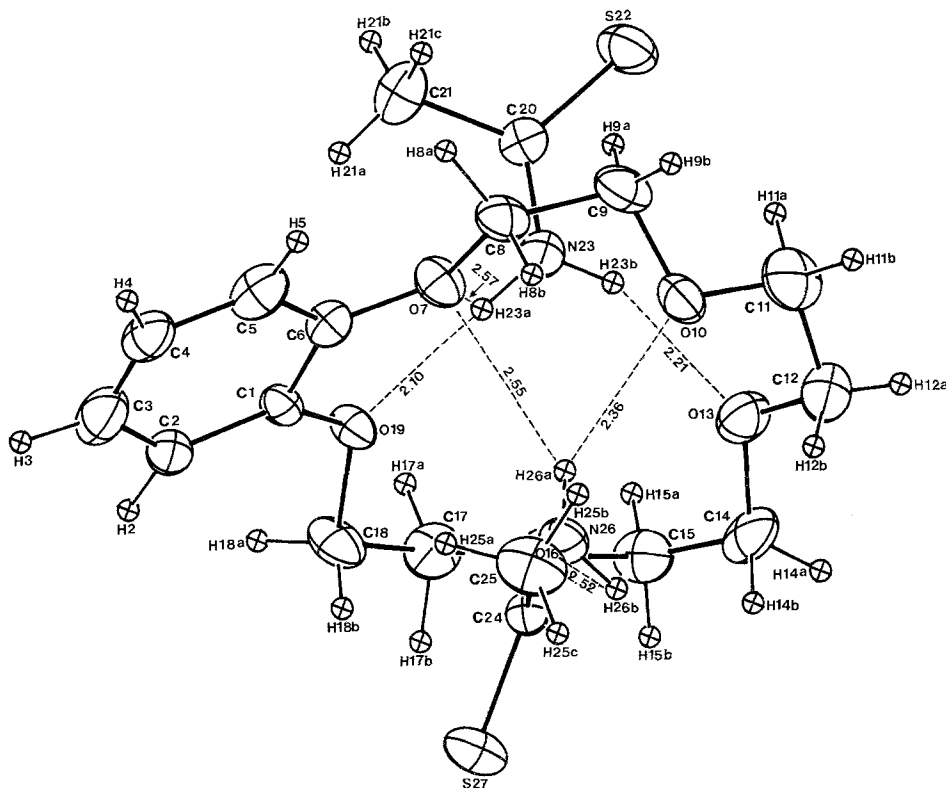


Fig. 2. Ortep drawing of the 1 : 2 complex between benzo-15-crown-5 and thioacetamide. O(16) is hidden beneath C(25) and N(26).

3. Molecular Mechanics

Conformational energies for the free benzo-15-crown-5 molecule were calculated by molecular mechanics techniques [8]. The X-ray parameters from complexes **1** and **2** were used as a starting set to locate a conformational minimum designated as **A**. The X-ray parameters for free crystalline benzo-15-crown-5 [7] were used as a starting set to generate conformation **B**. Both conformers **A** and **B** exhibit pseudo mirror planes passing through O(13) and bisecting the phenyl ring. This is consistent with the ^{13}C in which atoms related by the mirror plane show identical chemical shifts. The conformers differ primarily in the orientation of O(10) and O(16). In conformer **A** all O—C—O—O sequences exhibit *gauche* relationships except for that involving ortho attachment to the phenyl ring, and all C—O—C—C sequences approximate the energetically favored *anti* conformation. The average values for the two classes of torsion angles in **A** are 59° and 171° . In conformer **B** the O—C—C—O angles average 61° ; however, two C—O—C—C angles average 88° which differ significantly from the ideal value. When least-squares planes are fitted to the five oxygen atoms, the average deviations from the planes are 0.21 \AA for **A** and 0.24 \AA for **B**. The O...O perimeter distances are 2.71 and 2.75 \AA , respectively.

Molecular mechanics calculations predict **A** to be of lower energy by 2.61 kcal/mol which is primarily due to the torsional strain. This is reminiscent of the 18-crown-6 problem in which

Table IV. Bond distances (Å) and valence angles (°) for compounds 1 and 2

Atoms	1		2
C(1)—C(2)	1.368(5)		1.377(6)
C(1)—C(6)	1.392(3)		1.419(5)
C(1)—O(19)	1.386(4)		1.364(4)
C(2)—C(3)	1.404(6)		1.429(7)
C(3)—C(4)	1.379(5)		1.358(8)
C(4)—C(5)	1.369(6)		1.348(9)
C(5)—C(6)	1.405(4)		1.383(6)
C(6)—O(7)	1.362(4)		1.360(7)
O(7)—C(8)	1.442(3)		1.437(5)
C(8)—C(9)	1.490(5)		1.510(8)
C(9)—O(10)	1.407(4)		1.420(5)
O(10)—C(11)	1.420(5)		1.462(8)
C(11)—C(12)	1.508(5)		1.479(7)
C(12)—O(13)	1.425(4)		1.410(7)
O(13)—C(14)	1.418(3)		1.422(5)
C(14)—C(15)	1.491(6)		1.484(9)
C(15)—O(16)	1.420(4)		1.442(7)
O(16)—C(17)	1.397(5)		1.405(7)
C(17)—C(18)	1.524(5)		1.486(8)
C(18)—O(19)	1.423(3)		1.461(4)
N(20)—C(21)	1.337(4)	C(20)—C(21)	1.496(8)
C(21)—S(22)	1.635(4)	C(20)—S(22)	1.642(5)
C(21)—C(23)	1.517(4)	C(20)—N(23)	1.303(4)
C(23)—N(24)	1.319(4)	C(24)—C(25)	1.472(6)
C(23)—S(25)	1.661(4)	C(24)—N(26)	1.301(5)
		C(24)—S(27)	1.665(4)
C(2)—C(1)—C(6)	121.0(3)		119.9(3)
C(2)—C(1)—O(19)	124.0(2)		124.7(3)
C(6)—C(1)—O(19)	114.9(3)		115.3(2)
C(1)—C(2)—C(3)	119.3(3)		118.6(3)
C(2)—C(3)—C(4)	119.6(4)		120.4(6)
C(3)—C(4)—C(5)	121.3(4)		120.6(5)
C(4)—C(5)—C(6)	119.2(2)		121.9(4)
C(1)—C(6)—C(5)	119.3(3)		118.5(5)
C(1)—C(6)—O(7)	116.0(3)		114.6(3)
C(5)—C(6)—O(7)	124.6(2)		126.8(4)
C(6)—O(7)—C(8)	118.5(2)		117.6(3)
O(7)—C(8)—C(9)	107.5(2)		105.7(3)
C(8)—C(9)—O(10)	109.3(2)		109.0(3)
C(9)—O(10)—C(11)	113.5(2)		112.6(3)
O(10)—C(11)—C(12)	107.8(2)		109.0(4)
C(11)—C(12)—O(13)	106.1(3)		107.8(5)
C(12)—O(13)—C(14)	114.2(3)		114.8(3)
O(13)—C(14)—C(15)	106.6(3)		108.3(4)
C(14)—C(15)—O(16)	107.6(2)		107.3(4)
C(15)—O(16)—C(17)	114.1(2)		113.8(3)
O(16)—C(17)—C(18)	108.4(3)		108.6(4)
C(17)—C(18)—O(19)	106.5(2)		106.5(4)
C(1)—O(19)—C(18)	117.2(2)		117.0(3)
N(20)—C(21)—S(22)	125.5(2)	C(21)—C(20)—S(22)	119.4(3)
N(20)—C(21)—C(23)	111.9(3)	C(21)—C(20)—N(23)	116.7(4)
S(22)—C(21)—C(23)	122.6(2)	S(22)—C(20)—N(23)	123.9(4)
C(21)—C(23)—N(24)	112.9(3)	C(25)—C(24)—N(26)	115.4(3)
C(21)—C(23)—S(25)	122.4(2)	C(25)—C(24)—S(27)	121.5(3)
N(24)—C(23)—S(25)	124.6(2)	N(26)—C(24)—S(27)	123.1(3)

Table V. Selected torsion angles for 15-membered ring in benzo-15-crown-5

Angles	1	2	A ^a	3 ^b	B ^c
1-6-7-8	-172.4(3)	-168.4(3)	-163	-166	-174
6-7-8-9	175.4(3)	176.6(3)	172	171	177
7-8-9-10	-66.5(3)	-60.4(4)	-58	-71	-63
8-9-10-11	169.4(2)	171.4(4)	178	167	169
9-10-11-12	-154.0(3)	-162.8(4)	-170	-85	-88
10-11-12-13	65.0(3)	69.0(5)	59	-66	-58
11-12-13-14	-177.2(2)	-168.3(4)	-174	168	-179
12-13-14-15	179.9(3)	167.9(4)	175	-171	178
13-14-15-16	-68.4(3)	-65.1(4)	-59	72	61
14-15-16-17	168.3(2)	167.8(3)	171	81	89
15-16-17-18	-168.6(2)	-176.1(3)	-178	-163	-168
16-17-18-19	64.6(3)	64.8(4)	58	70	62
17-18-19-6	-168.2(3)	-173.8(3)	-190	-170	-172
18-19-6-1	155.2(3)	154.4(3)	160	-167	168
19-6-1-7	-0.9(4)	-0.8(4)	0	0	0

^a A, Calculated using 1 and 2 as starting parameters.

^b 3, Conformation in crystalline benzo-15-crown-5 [7].

^c B, Calculated using 3 as starting parameters.

Table VI. Potential interactions between crown oxygen atoms and N—H groups. Distances are measured in Å and angles in degrees

Complex 1

N(20)—H(20a) = 1.06(4)	H(20a)···O(13) = 2.09(4)	N(20)···O(13) = 3.004(4)	N(20)—H(20a)···O(13) = 144(1)
N(20)—H(20b) = 0.89(4)	H(20b)···O(19) = 2.10(4)	N(20)···O(19) = 2.987(4)	N(20)—H(20b)···O(19) = 173(1)
N(20)—H(20b) = 0.89(4)	H(20b)···O(7) = 2.56(4)	N(20)···O(7) = 2.068(4)	N(20)—H(20b)···O(7) = 117(1)
N(24)—H(24a) = 0.92(4)	H(24a)···O(10') = 2.37(4)	N(24)···O(10') = 3.201(4)	N(24)—H(24a)···O(10') = 51(1)
N(24)—H(24a) = 0.92(4)	H(24a)···O(13') = 2.65(4)	N(24)···O(13') = 3.445(4)	N(24)—H(24a)···O(23') = 145(1)
N(24)—H(24b) = 0.89(4)	H(24b)···O(7') = 2.77(4)	N(24)···O(7') = 3.167(4)	N(24)—H(24b)···O(17') = 109(1)

Complex 2

N(23)—H(23a) = 0.97(5)	H(23a)···O(19) = 2.10(5)	N(23)···O(19) = 3.074(6)	N(23)—H(23a)···O(19) = 179(1)
N(23)—H(23a) = 0.97(5)	H(23a)···O(7) = 2.57(5)	N(23)···O(7) = 3.085(6)	N(23)—H(23a)···O(7) = 114(1)
N(23)—H(23b) = 0.87(5)	H(23b)···O(13) = 2.21(5)	N(23)···O(13) = 2.960(6)	N(23)—H(23b)···O(13) = 144(1)
N(26)—H(26a) = 0.89(5)	H(26a)···O(10) = 2.36(5)	N(26)···O(10) = 2.994(6)	N(26)—H(26a)···O(10) = 128(1)
N(26)—H(26a) = 0.89(5)	H(26a)···O(7) = 2.55(5)	N(26)···O(7) = 3.197(6)	N(26)—H(26a)···O(7) = 130(1)
N(26)—H(26b) = 0.95(5)	H(26b)···O(16) = 2.52(5)	N(26)···O(16) = 2.900(6)	N(26)—H(26b)···O(16) = 104(1)

normal molecular mechanics calculations indicate the D_{3d} conformer to be of lower energy; however, proper treatment of atomic charge distributions led to a reversal of energies and the conformer observed in the solid state was of lowest energy [3, 9]. Charges as large as $-0.600 e$ and $+0.300 e$ were assigned to the oxygen and carbon atoms in the benzo-15-crown-5 case; however, no reversal of energies occurred. Either molecular mechanics is not reliable for this system or benzo-15-crown-5 crystallizes as the less stable conformer. Room temperature ^1H and ^{13}C NMR spectra gave sharp lines with no indication of a conformer mixture. Since the conformational barrier is primarily the energy required to go from a C—O—C—C torsion angle of 170° to 88° the two levels should be thermally accessible.

4. Discussion

Figures 1 and 2 show the structures of the complexes **1** and **2**, respectively. The benzo-15-crown-5 host adopt conformation **A** in the two complexes. The O—C—C—O torsion angles average 66(2) and 65(2)° in the two complexes while the C—O—C—C angles approximate the energetically favorable *anti* arrangement with average values of 169° in the two structures. The torsion angles adjacent to the phenyl rings are reduced to 155.2(3)° and 154.4(3)° in the two structures while the C(9)—O(10)—C(11)—C(12) angles are -154.0(3) and -162.8(4)°. These differences probably arise from accommodations to hydrogen bonding rather than intermolecular packing interactions. The five oxygen atoms of the crown form an approximate pentagon with maximum deviations from the planes of 0.3 Å in the observed structures. Four sides of the pentagon average 2.78 Å in the two structures while the fifth side adjacent to the phenyl ring is reduced to 2.56 Å. The calculated values of 2.72 and 2.65 Å for the **A** conformation are more nearly equal. Interactions across the rings range from 4.15 to 4.58 Å in the two complexes and from 4.31 to 4.39 and 4.11 to 4.54 Å for conformers **A** and **B**, respectively. Conformation **A** is observed for the Na⁺ complex of benzo-15-crown-5 [10] and for a water coordinated free host in a Ca²⁺ complex crystal [11]. The Ca²⁺ complexed host exhibits conformation **B**.

4.1. 1:1 BENZO-15-CROWN-5: DITHIOOXAMIDE COMPLEX, **1**

The crystal contains long chains of alternating host-guest-host-guest molecules. The chains are held together by van der Waals interactions. The dithiooxamide molecule is twisted slightly from planarity to accommodate hydrogen bond formation, N(20)—C(21)—C(23)—N(24) = -165.4(3)°. The dihedral angle between the mean plane of the oxygen pentagon and the dithiooxamide molecule is 85(1)° while the angle between the crown plane and the phenyl ring is 26(1)°. N(20) and N(24) lie 2.18(1) and 2.19(1) Å out of the plane of the oxygen atoms. The O⋯H(N) distances range from 2.09(4) to 2.77(3) Å indicating a distribution of interaction energies. O(16) is not involved in hydrogen bonding while O(7) and O(13) interact with hydrogen atoms on both sides of the plane. While the H(24c)⋯O(10') distance is 2.37(4) Å the N(24)—H(24a)⋯O(10') angle is only 51(1)°.

4.2. 1:2 BENZO-15-CROWN-5: THIOACETAMIDE, **2**

The solid contains discrete units of the complex formed by the interaction of the crown with two thioacetamide molecules from opposite sides. The isolated complexes then interact via van der Waals forces. The thioacetamide molecules are planar and form interplanar angles of 62 and 67° with the mean plane of the five oxygen atoms and 77° with each other. N(23) and N(26) lie 2.18(1) and 2.15(1) Å out of this plane which are identical to the distances in **1**. One amide hydrogen bisects one side of the pentagon forming a bifurcated hydrogen-like bond while the other points directly toward the opposite apex forming a single hydrogen⋯oxygen interaction. Three hydrogen interactions occur on each face. The O⋯H distances range from 2.10 to 2.57 Å indicating a reasonably good fit between the host and guest molecules.

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