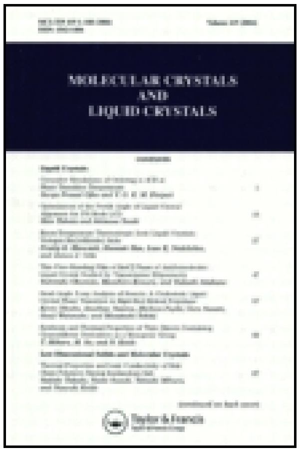

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Crystal and Molecular Structure Studies of Some Organic Haloamines

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Crystal and Molecular Structure Studies of some Organic Haloamines

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Sodium salt of *N*-bromobenzenesulfonamide, $C_6H_5SO_2NBrNa\ 1.5H_2O$, $F.W = 282.07$, monoclinic, $P2_1/c$, $a = 10.499(3)$ Å, $b = 6.750(4)$ Å, $c = 11.802(6)$ Å, $\beta = 104.08(3)°$, $V = 1017.4(8)$ Å^3, $Z = 4$, $D_{calc} = 1.841\ \mathrm{gm\,cm^{-3}}$, $\mu = 4.267\ \mathrm{cm^{-1}}$, $F_{000} = 552$, $\lambda(\mathrm{MoK}\alpha) = 0.71069$ Å, final $R1$ and $\omega R2$ are 0.116 and 0.279 respectively. The crystal structure shows the dominant motif which can be described as an aquo-bridged sodium dimer (Na—O = 2.4382(2)Å, 2.4392(1) Å). In addition to the bridging of water molecules, the halves of the dimer are held together by a hydrogen bond between a coordinated water molecule and the amido nitrogen.

N,N'-dibromobenzenesulfonamide, $C_6H_5SO_2NBr_2$, $F.W = 314.98$, monoclinic, $P2_1/c$, $a = 10.518(5)$ Å, $b = 8.10(1)$ Å, $c = 11.812(6)$ Å, $\beta = 112.83(4)°$, $V = 926(1)$ Å^3, $Z = 4$, $D_{calc} = 1.26\ \mathrm{gm\,cm^{-3}}$, $\mu = 8.95\ \mathrm{cm^{-1}}$, $F_{000} = 600$, $\lambda(\mathrm{MoK}\alpha) = 0.71069$ Å, final R and R_ω are 0.069 and 0.079 respectively.

N,N'-dichlorobenzenesulfonamide, $C_6H_5SO_2NCl_2$, $F.W = 226.08$, monoclinic, $P2_1/c$, $a = 10.42(1)$ Å, $b = 8.098(8)$ Å, $c = 11.697(7)$ Å, $\beta = 113.03(4)°$, $V = 908(1)$ Å^3, $Z = 4$, $D_{calc} = 1.65\ \mathrm{gm\,cm^{-3}}$, $\mu = 8.94\ \mathrm{cm^{-1}}$, $F_{000} = 456$, $\lambda(\mathrm{MoK}\alpha) = 0.71069$ Å, final R and R_ω are 0.04 and 0.044 respectively.

N,N'-dichloro-4-methylbenzenesulfonamide, $C_7H_7SO_2NCl_2$, $F.W = 240.10$, monoclinic, $P2_1/n$, $a = 7.179(3)$ Å, $b = 16.217(2)$ Å, $c = 8.692(3)$ Å, $\beta = 96.69(3)°$, $V = 1005.1(4)$ Å^3, $Z = 4$, $D_{calc} = 1.598\ \mathrm{gm\,cm^{-3}}$, $\mu = 8.2\ \mathrm{cm^{-1}}$, $F_{000} = 488$, $\lambda(\mathrm{MoK}\alpha) = 0.71069$ Å, final R and R_ω are 0.055 and 0.079 respectively.

Keywords: Crystal structure; bromamine-B; DBB; DCB; DCT

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INTRODUCTION

The diverse nature of the chemistry of aromatic sulfonyl haloamines is due to their ability to act as sources of halonium cations, hypohalite species and *N*-anions which act as both bases and nucleophiles. As a result, these reagents react with a wide range of functional groups effecting an array of molecular transformations. These reagents have been extensively used as chlorinating/brominating/oxidizing agents in synthetic chemistry. Also, they are widely used in the analytical determination of various organic and inorganic substrates. A recent review [1] on organic haloamines reveals that except for the work of crystal structure of chloramine-T [2], crystal structures of other compounds like chloramine-B, bromamine-T, bromanine-B, iodamine-T, iodamine-B and their dihalo compounds have not been studied.

The reactions of *p*-nitrophenoxide ion [3], indigocarmine [4], glutamic acid and its rare earth complexes [5], caffeine [6], dimethylsulphoxide [7], ethylphenylthioacetates [8], diphenylsulphoxide [9], monosaccharides [10], substituted benzyl alcohols [11], diols [12] and aliphatic aldehydes [13] and indoles [14] with bromamine-B (BAB) have been reported.

The reaction of dibromamine-B (DBB) with cyclohexene [15], cyclopentene [16], trichloropropene [17], olefins [18], acetophenones [19] and styrene [20] have been reported. Suketaka and Toshio [21] have studied the bromination of hydrocarbons using DBB. Oxidation of ether by DBB [22, 23] and kinetics of the reaction of tetrahydrofuran with DBB [24] have been reported. Gottardi [25] has studied the substitution reaction of DBB with iodine. Analytical determination of cyanide [26], thiocyanate [27], thiosemicarbazide [27] various inorganic and organic compounds [28] have been carried out with DBB.

Our recent work on the photolysis of aqueous bromamine-B under UV light radiation produces DBB as one of the major products [29]. Also, our work on the interaction of ZR(IV) and Th(IV) solutions with aqueous bromamine-B produces DBB [30]. The reactions of unsaturated alcohols [31], isoniazid [32], methionine and its complexes [33], thiocyanate ion [34], semicarbazide [35] and aminoacids [36] with dichloramine-B (DCB) have been reported. The reactions of aldehydes [37], glutathione [38], thioacetamide [39], isoniazid [32], aniline [40], aminoacids [41] and styrene derivatives [42] with dichloramine-T (DCT) have been studied.

The crystal structures of sodium salt of *N*-bromobenzenesulfonamide (BAB), *N*,*N*′-dibromobenzenesulfonamide (DBB), *N*-*N*′-dichlorobenzenesulfonamide (DCB), and *N*,*N*′-dichloro-4-methylbenzenesulfonamide

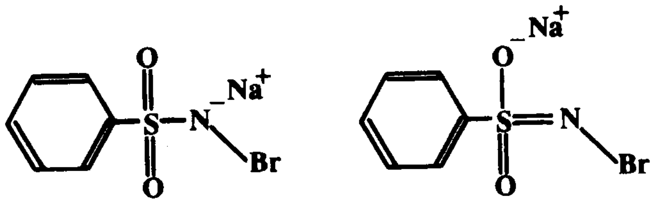
(DCT) are still lacking. In view of the importance of these compounds in reaction kinetics, synthetic as well as analytical work, it is worthwhile to investigate the crystal and molecular structures of these organic haloamines.

CRYSTAL DATA, X-RAY DATA COLLECTION AND SOLUTION AND REFINEMENT OF STRUCTURE

Crystal Structure of BAB

X-ray crystallographic study of bromamine-B indicates there is no interaction between nitrogen and sodium. Instead, the Na^+ ion interacts with one of the sulfonyl oxygens and a bromine from a neighbouring ion. The Na^+ coordination sphere involves oxygens from waters of crystallization. The structure of bromamine-B is therefore closer to the formulation **B** than to its more common representation **A** as shown in Figure 1.

A yellow rectangular crystal of dimension 0.1 × 0.2 ×0.2 mm was selected for X-ray data collection. All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated (Mo-$K\alpha$) radiation. The data were collected at a temperature of 293 K using the ω-2θ scan technique. Least-squares refinement of 25 reflections in the range $14.28 < 2\theta < 17.82°$ yielded a primitive monoclinic cell with demensions $a = 10.499(3)$ Å, $b = 6.750(4)$ Å, $c = 11.802(6)$ Å, $\beta = 104.08(3)°$, $V = 1017.4(8)$ Å^3, $Z = 4$, $F.W = 282.07$, $D_{\text{calc}} = 1.841$ gm cm^{-3}, $F_{000} = 552$, space group $P2_1/c$ and $\mu(\text{MoK}\alpha) = 4.267$ cm^{-1}. An empirical absorption correction [45] based on azimuthal scans of three reflections was applied which resulted in the transmission factors ranging from 0.86 to 1.00. A total of 1042 intensities were collected in the range of $0 \leq 2\theta \leq 50°$ of which 984 were unique



A **B**

FIGURE 1

($R_{\mathrm{int}} = 0.13$). The structure was solved by direct methods (SIR92) [46] and the resulting fragment was expanded using difference Fourier maps. The function minimized throughout refinement was $\Sigma\omega(|F_o| - |F_c|)^2$ with $\omega = 1/\sigma^2(F_o)$. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and were not refined. The final cycle of full-matrix refinement [47] was based on 854 observed reflections ($I > 2\sigma(I)$) and 124 parameters and converged to $R1 = 0.116$, $\omega R2 = 0.279$ with goodness of fit = 1.021.

Results and Discussion

The positional parameters and equivalent temperature factors for non-hydrogen atoms are given in Table I. Anisotropic parameters (U_{ij}) are listed in Table II. Bond distances and bond angles are given in Tables III and IV respectively. Figure 2 represents the ORTEP diagram of the BAB molecule with thermal ellipsoids at 50% probability. Packing of the molecules down *b* axis is shown in Figure 3. The compound shows stacking of molecules along *a* axis. The crystal structure shows the dominant motif which can be described as an aquo-bridged sodium dimer (Na—O = 2.4382(2)Å, 2.4392(1) Å). In addition to the bridging of water molecules, the halves of the dimer are held together by a hydrogen bond between a coordinated water molecule and the amido nitrogen.

A different dimer related by inversion, provides additional hydrogen bonds to N, O(1), O(4) and O(3). Thus, each hydrogen belonging to water

TABLE I Atomic coordinates, equivalent isotropic displacement parameters (Å^2) of BAB

Atom	*x*	*y*	*z*	*U(eq)*
Br1	0.1396(2)	−0.9243(2)	0.25085(13)	0.0682(12)
S1	0.1593(4)	−0.5472(7)	0.1667(3)	0.0449(13)
Na1	0.1372(7)	−0.2620(13)	−0.0375(5)	0.055(2)
O3	0.0000	0.0019(42)	0.0000	0.061(5)
O4	0.3015(13)	−0.0848(21)	0.0820(10)	0.059(3)
O2	0.0843(11)	−0.4031(27)	0.1007(8)	0.054(3)
O1	0.2874(11)	−0.5877(25)	0.1548(9)	0.058(3)
N1	0.0634(15)	−0.7254(26)	0.1609(9)	0.051(3)
C1	0.3018(23)	−0.3702(49)	0.3278(14)	0.080(8)
C2	0.3138(42)	−0.2892(60)	0.4104(23)	0.111(11)
C3	0.1999(44)	−0.2616(40)	0.4508(22)	0.112(13)
C4	0.0810(35)	−0.3158(44)	0.3971(18)	0.090(9)
C5	0.0748(25)	−0.3992(59)	0.3144(17)	0.079(7)
C6	0.1827(18)	−0.4398(26)	0.2765(11)	0.050(4)

TABLE II Anisotropic displacement parameters (Å^2) for non-hydrogen atoms of BAB

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br1	0.084(2)	0.0523(15)	0.068(2)	0.0145(10)	0.0181(9)	0.0068(11)
S1	0.046(2)	0.044(2)	0.041(2)	−0.001(2)	0.0039(13)	0.002(2)
Na1	0.055(3)	0.052(5)	0.059(4)	0.001(4)	0.014(3)	−0.004(3)
O3	0.050(9)	0.066(14)	0.063(10)	0.000	0.003(7)	0.000
O4	0.058(6)	0.038(6)	0.075(8)	0.015(6)	0.007(6)	−0.006(5)
O2	0.059(6)	0.056(8)	0.045(5)	0.014(7)	0.006(4)	0.002(6)
O1	0.043(5)	0.070(9)	0.064(7)	−0.002(7)	0.022(5)	0.005(6)
N1	0.066(8)	0.047(9)	0.034(6)	0.002(6)	−0.001(5)	0.001(7)
C1	0.078(12)	0.100(23)	0.051(10)	−0.016(12)	−0.007(9)	−0.013(14)
C2	0.139(28)	0.082(21)	0.093(18)	−0.013(20)	−0.011(19)	−0.031(22)
C3	0.196(39)	0.035(13)	0.091(18)	−0.021(14)	0.006(24)	−0.011(19)
C4	0.150(24)	0.066(16)	0.073(14)	−0.009(13)	0.063(16)	0.029(18)
C5	0.086(13)	0.086(19)	0.069(11)	0.013(15)	0.027(10)	−0.006(14)
C6	0.070(9)	0.025(7)	0.050(8)	0.009(8)	0.007(7)	0.002(8)

TABLE III Bond lengths (Å) of BAB

Atom	*Atom*	*Distance*	*Atom*	*Atom*	*Distance*
Br1	N1	1.92(2)	S1	O1	1.424(11)
S1	O2	1.465(15)	S1	N1	1.56(2)
S1	C6	1.74(2)	Na1	O3	2.44(2)
Na1	O2	2.439(14)	Na1	O4	2.459(14)
C1	C2	1.32(4)	C1	C6	1.38(3)
C2	C3	1.47(6)	C3	C4	1.36(5)
C4	C5	1.33(4)	C5	C6	1.41(3)

TABLE IV Bond Angles (°) of BAB

Atom	*Atom*	*Atom*	*Angle*	*Atom*	*Atom*	*Atom*	*Angle*
O1	S1	O2	114.5(8)	O1	S1	N1	117.5(10)
O2	S1	N1	103.9(8)	O1	S1	C6	105.8(8)
O2	S1	C6	106.0(8)	N1	S1	C6	108.4(8)
O3	Na1	O2	80.0(6)	O3	Na1	O4	80.3(5)
O2	Na1	O4	81.4(5)	S1	O2	Na1	128.5(8)
S1	N1	Br1	110.3(8)	C2	C1	C6	121.5(27)
C1	C2	C3	121.7(29)	C4	C3	C2	116.7(27)
C5	C4	C3	119.0(30)	C4	C5	C6	125.7(26)
C1	C6	C5	115.1(21)	C1	C6	S1	124.0(16)
C5	C6	S1	120.6(17)				

molecule is involved in some type of hydrogen bonding, while each water oxygen, as well as the nitrogen atom, have two hydrogen bonded contacts. In addition, O(1), a sulfonyl oxygen, has two hydrogen bonds, but O(2) has none, as it is involved in coordination to the sodium. ***N-Sodio*** interaction is clearly a misnomer, at least in the solid state. The closest N. . .Na distance is 4.487(1) Å, and it involves the nitrogen bonded to the coordinated bromine.

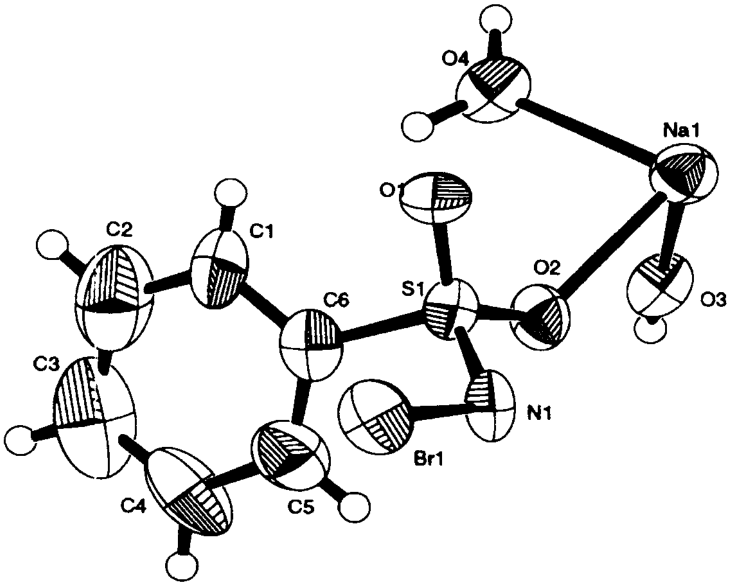


FIGURE 2 ORTEP diagram of BAB.

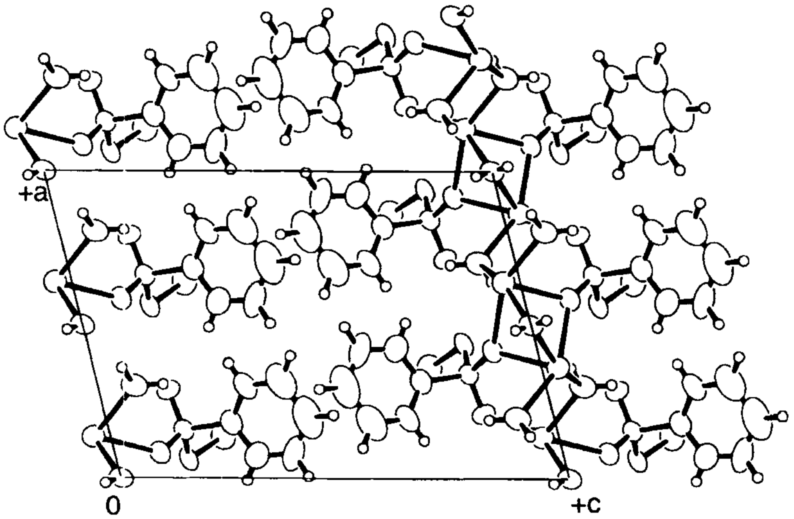


FIGURE 3 Packing of molecules down *b*-axis (BAB).

The tetrahedral geometry around sodium is fairly regular. The three NaO bonds range from 2.4382(2) Å to 2.4392(1) Å and the largest deviation from the idealized octahedral angle is 111.2(1) Å for O(2)—Na—O(1). This geometry is comparable to that found in sodium acetylacetonate monohydrate.

As per our knowledge, the structure of the $R\mathrm{SO_2NBr^-}$ grouping is reported here for the first time. Support of formulation **B** for the structure of its sodium salt comes from three major structural features: (i) the only interaction between sodium and the $\mathrm{SO_2N}$ moiety involves a Na—O rather than Na—N contact. (ii) The S—N distance 1.5379(1) Å is consistent with a double rather than a single bond. (iii) aggregation is a result of the tendency of the $\mathrm{Na^+}$ ion to achieve 6-coordination, which it does through coordination to one sulfonyl oxygen only; two bridging and two terminal waters and a bromine from another bromamine-B molecule comprise the rest of the coordination sphere. This in turn gives rise to several hydrogen bonding contacts between water hydrogens and oxygen and nitrogen atoms. Clearly, then the aggregation seems to have no significant effect on the structure of the $i[\mathrm{C_6H_5SO_2NBr}]^-$ ion. The molecules are stacked in layers with parts of phenyl rings separated by water and sodium groups.

In summary, the best description of bromamine-B is that its structure is close to that depicted in **B** rather than its more common representation of **A** as shown in Figure 1.

Crystal Structure of DBB

A yellow rectangular crystal of dimension 0.1 × 0.2 × 0.5 mm was selected for X-ray data collection. All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated (Mo-Kα) radiation. The data were collected at a temperature of 293 °K using the ω-2θ scan technique.

Least-squares refinement of 25 reflections in the range $13.82 < 2\theta < 17.91°$ yielded to a primitive monoclinic cell with dimensions $a = 10.518(5)$ Å, $b = 8.10(1)$ Å, $c = 11.812(6)$ Å, $\beta = 112.83(4)°$, $V = 926(1)$ Å^3, $Z = 4$, $F.W. = 314.98$, $D_{\mathrm{calc}} = 1.26\,\mathrm{gm\,cm^{-3}}$, $F_{000} = 600$, space group $P2_1/c$ and $\mu(\mathrm{MoK}\alpha) = 8.95\,\mathrm{cm^{-1}}$. The data were corrected for Lorentz and polarization effects. A total of 1860 data were collected in the range of $0 \leq 2\theta \leq 50°$ of which 1761 were unique ($R_{\mathrm{int}} = 0.13$). The structure was solved by direct methods (SIR92) [46] and expanded using difference Fourier maps [48]. An absorption correction (DIFABS [49]) was applied resulting in transmission factors ranging from 0.54–1.0000. The function minimized throughout refinement was $\Sigma\omega(|F_o| - |F_c|)^2$ with $\omega = 1/\sigma^2(F_o)$. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed at the calculated positions and were not refined. The final cycle of full-matrix refinement

[48] based on 721 observed reflections ($I > 3\sigma(I)$) and 130 parameters converged to $R = 0.069$, $R_\omega = 0.079$ with goodness of fit = 2.28.

Results and Discussion

The positional parameters and equivalent temperature factors for non-hydrogen atoms are given in Table V. Anisotropic parameters (U_{ij}) are listed in Table VI. Bond distances and bond angles are given in Tables VII and VIII respectively. Figure 4 represents the ORTEP diagram of the DBB molecule at 50% probability. Figures 5 and 6 show that packing of molecules in the unit cell down *b* and *c* axes respectively. Stacking of molecules can be observed along the *a* axis in both the cases.

The bond distances of S(7)—O(8) and S(7)—O(9) are 1.4234(1) Å and 1.4290(2) Å, which are well within the range of similar molecules whose structures have been reported earlier [2]. The phenyl ring is quite normal,

TABLE V Atomic coordinates and B_{iso}/B_{eq} of DBB

Atom	*x*	*y*	*z*	B_{eq}
Br(11)	0.0543(3)	0.7798(3)	0.4944(2)	6.59(8)
Br(12)	−0.0016(3)	0.5528(3)	0.2684(2)	5.72(7)
S(7)	0.2822(6)	0.6776(6)	0.4175(5)	3.3(1)
O(8)	0.348(1)	0.821(2)	0.484(1)	5.0(4)
O(9)	0.302(1)	0.629(2)	0.309(1)	4.5(4)
N(10)	0.108(2)	0.724(2)	0.362(1)	4.2(4)
C(1)	0.297(2)	0.353(3)	0.467(2)	3.6(6)
C(2)	0.321(2)	0.221(3)	0.548(2)	4.6(7)
C(3)	0.355(2)	0.249(4)	0.671(2)	5.3(7)
C(4)	0.366(3)	0.402(3)	0.720(2)	4.9(7)
C(5)	0.345(2)	0.539(3)	0.639(2)	3.4(6)
C(6)	0.311(2)	0.507(2)	0.518(2)	2.9(5)

TABLE VI Anisotropic displacement parameters (Å^2) for non-hydrogen atoms of DBB

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br (11)	0.117(2)	0.083(2)	0.074(2)	0.040(2)	0.064(2)	0.009(2)
Br(12)	0.081(2)	0.076(2)	0.050(2)	−0.007(2)	0.014(1)	0.005(1)
S(7)	0.070(4)	0.025(3)	0.043(3)	−0.002(3)	0.034(3)	0.003(3)
O(8)	0.09(1)	0.035(9)	0.07(1)	−0.016(9)	0.032(9)	−0.001(8)
O(9)	0.10(1)	0.045(8)	0.051(9)	0.003(8)	0.060(9)	−0.002(8)
N(10)	0.09(1)	0.05(1)	0.027(9)	0.00(1)	0.036(9)	0.008(8)
C(1)	0.08(2)	0.04(1)	0.03(1)	0.01(1)	0.03(1)	0.01(1)
C(2)	0.07(2)	0.03(1)	0.08(2)	−0.00(1)	0.04(1)	−0.02(1)
C(3)	0.06(1)	0.10(2)	0.05(2)	0.03(2)	0.03(1)	0.03(2)
C(4)	0.09(2)	0.06(2)	0.05(2)	0.01(2)	0.04(2)	0.02(1)
C(5)	0.07(1)	0.02(1)	0.05(1)	−0.00(1)	0.03(1)	−0.01(1)
C(6)	0.07(1)	0.02(1)	0.04(1)	0.01(1)	0.04(1)	0.001(9)

TABLE VII Bond lengths (Å) of DBB

Atom	*Atom*	*Distance*	*Atom*	*Atom*	*Distance*
Br(11)	N(10)	1.91(1)	C(1)	C(2)	1.39(3)
Br(12)	N(10)	1.87(2)	C(1)	C(6)	1.37(2)
S(7)	O(8)	1.42(1)	C(2)	C(3)	1.37(3)
S(7)	O(9)	1.43(1)	C(3)	C(4)	1.35(3)
S(7)	N(10)	1.73(2)	C(4)	C(5)	1.42(3)
S(7)	C(6)	1.77(2)	C(5)	C(6)	1.36(2)

TABLE VIII Bond angles (°) of DBB

Atom	*Atom*	*Atom*	*Angle*	*Atom*	*Atom*	*Atom*	*Angle*
O(8)	S(7)	O(9)	120.9(9)	C(2)	C(1)	C(6)	116(2)
O(8)	S(7)	N(10)	104.4(8)	C(1)	C(2)	C(3)	120(2)
O(8)	S(7)	C(6)	110.0(9)	C(2)	C(3)	C(4)	123(3)
O(9)	S(7)	N(10)	102.8(8)	C(3)	C(4)	C(5)	118(2)
O(9)	S(7)	C(6)	110.0(8)	C(4)	C(5)	C(6)	118(2)
N(10)	S(7)	C(6)	107.6(8)	S(7)	C(6)	C(1)	117(1)
Br(11)	N(10)	Br(12)	110.6(8)	S(7)	C(6)	C(5)	118(1)
Br(11)	N(10)	S(7)	110.5(8)	C(1)	C(6)	C(5)	125(2)
Br(12)	N(10)	S(7)	112.6(9)				

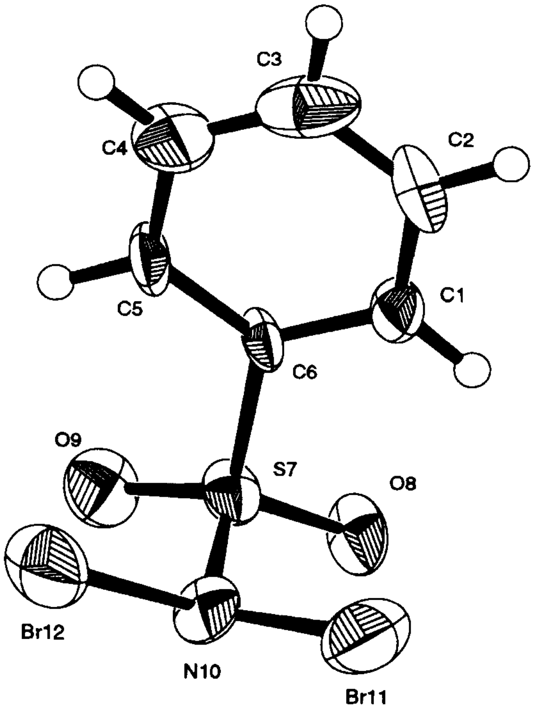


FIGURE 4 ORTEP diagram of DBB.

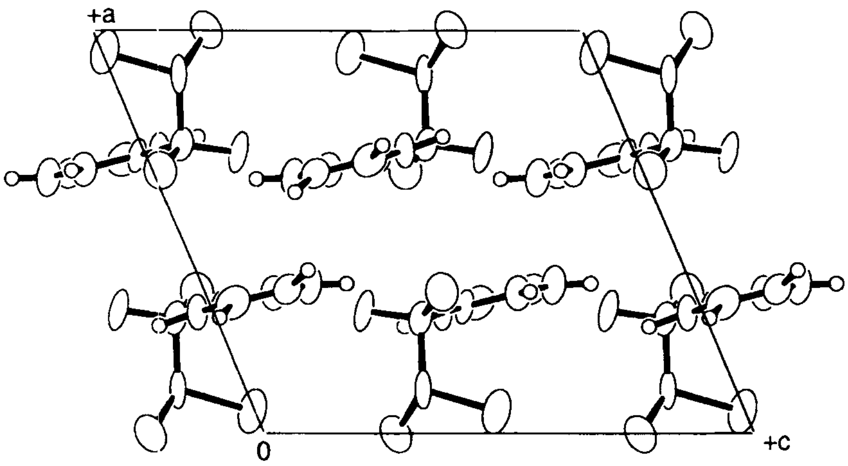


FIGURE 5 Packing of molecules down *b*-axis (DBB).

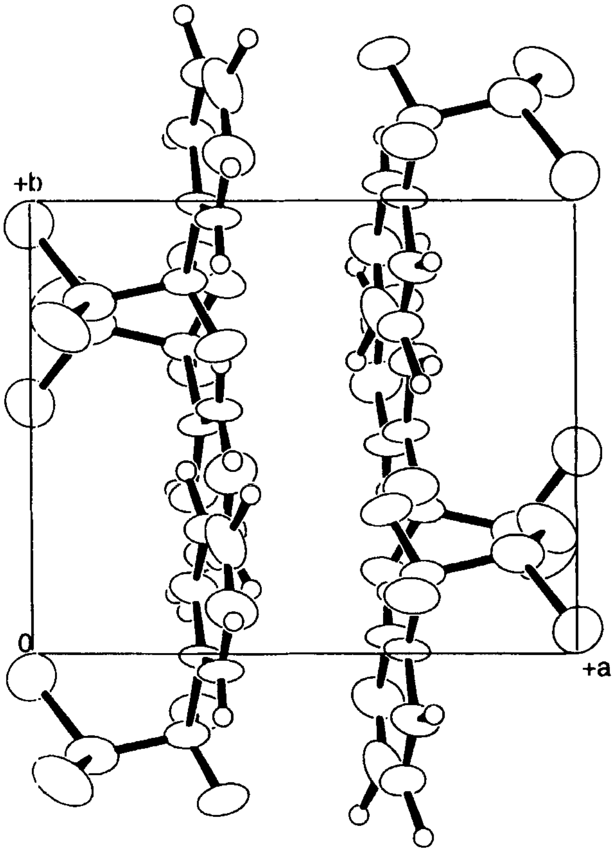


FIGURE 6 Packing of molecules down *c*-axis (DBB).

with mean ring C—C bond of 1.377(2) Å and an average deviation of 0.008 Å. The N—Br distance is 1.9098(1) Å. And hydrogen bonding can be observed between the following atoms. C(5)—H...O(8) = 2.595(1) Å, C(1)—H...O(9) = 2.382(1) Å, C(5)—H...Br(11) = 3.177(1) Å, C(1)—H...Br(12) = 2.988(1) Å. Intra molecular bonding between O and Br is observed with an average bond length of 3.127(1) Å.

Crystal Structure of DCB

A yellow rectangular crystal of approximate dimension 0.1 × 0.15 × 0.2 mm was selected for data collection. All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated radiation. The data were collected at a temperature of 293 K using the ω-2θ scan technique. Least-squares refinement of 25 reflections in the range $14.23 < 2\theta < 17.31°$ yielded a primitive monoclinic cell with dimensions $a = 10.42(1)$ Å, $b = 8.098(8)$ Å, $c = 11.697(7)$ Å, $\beta = 113.03(4)°$, $V = 908(1)$ Å^3, $Z = 4$, $F.W = 226.08$, $D_{\text{calc}} = 1.65$ gm cm^{-3}, $F_{000} = 456$, space group $P2_1/c$ and μ(MoKα) = 8.94 cm^{-1}. An empirical absorption correction [45] based on azimuthal scans of three reflections was applied which resulted in the transmission factors ranging from 0.8959 to 1.00. A total of 1485 intensities were collected in the range of $0 \leq 2\theta \leq 50°$ of which 1405 were unique ($R_{\text{int}} = 0.028$). The structure was solved by direct methods (SIR92) [46] and expanded using difference Fourier maps [48]. The function minimized throughout refinement was $\Sigma\omega(|F_o| - |F_c|)^2$ with $\omega = 1/\sigma^2(F_o)$. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed at the calculated positions and were not refined. The final cycle of full-matrix refinement [48] based on 979 observed reflections ($I > 3\sigma(I)$) and 110 variable parameters converged to $R = 0.04$, $R_\omega = 0.044$ with goodness of fit = 3.78.

Results and Discussion

The positional parameters and equivalent temperature factors for non-hydrogen atoms are given in Table IX. Anisotropic parameters (U_{ij}) are listed in Table X. Bond distances and bond angles are given in Tables XI and XII respectively. Figure 7 represents the ORTEP diagram of the DCB molecule at 50% probability. Figures 8 and 9 show packing of molecules in the unit cell down *b*- and *c*-axes respectively. Stacking of molecules along *a*-axis can be observed in both the cases. This is similar to the earlier case of

TABLE IX Atomatic coordinates and B_{iso}/B_{eq} of DBB

Atom	*x*	*y*	*z*	B_{eq}
Cl(11)	0.5626(1)	0.2895(2)	0.4861(1)	8.04(4)
Cl(12)	0.4969(1)	0.0719(2)	0.2816(1)	8.43(4)
S(7)	0.7775(1)	0.1761(1)	0.41214(9)	4.08(3)
O(8)	0.8481(3)	0.3182(3)	0.4768(3)	5.84(8)
O(9)	0.7893(3)	0.1253(3)	0.3006(2)	6.16(9)
N(10)	0.6030(3)	0.2336(4)	0.3619(3)	5.17(9)
C(1)	0.7851(4)	−0.1483(5)	0.4650(4)	4.4(1)
C(2)	0.8079(5)	−0.2794(5)	0.5447(5)	5.7(1)
C(3)	0.8479(5)	−0.2528(6)	0.6699(5)	5.8(1)
C(4)	0.8661(5)	−0.0949(7)	0.7169(4)	5.7(1)
C(5)	0.8429(4)	0.0384(5)	0.6391(4)	4.4(1)
C(6)	0.8038(4)	0.0092(4)	0.5127(3)	3.37(9)

TABLE X Anisotropic displacement parameters (Å^2) for non-hydrogen atoms of DCB

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(11)	0.108(1)	0.102(1)	0.118(1)	0.0457(9)	0.0695(9)	0.0134(9)
Cl(12)	0.0761(9)	0.102(1)	0.102(1)	−0.0098(8)	−0.0093(7)	0.0077(9)
S(7)	0.0660(7)	0.0380(6)	0.0573(7)	0.0019(5)	0.0311(5)	0.0040(5)
O(8)	0.087(2)	0.039(2)	0.096(2)	−0.013(2)	0.036(2)	−0.005(2)
O(9)	0.124(3)	0.070(2)	0.065(2)	0.009(2)	0.064(2)	0.010(2)
N(10)	0.070(2)	0.055(2)	0.064(2)	0.010(2)	0.019(2)	0.011(2)
C(1)	0.075(3)	0.037(2)	0.064(3)	0.006(2)	0.037(2)	−0.001(2)
C(2)	0.087(4)	0.039(3)	0.109(4)	0.008(2)	0.056(3)	0.007(3)
C(3)	0.065(3)	0.071(3)	0.093(4)	0.021(3)	0.040(3)	0.038(3)
C(4)	0.063(3)	0.099(4)	0.052(3)	0.010(3)	0.019(2)	0.024(3)
C(5)	0.053(2)	0.057(3)	0.050(3)	−0.002(2)	0.015(2)	−0.002(2)
C(6)	0.043(2)	0.038(2)	0.051(3)	0.005(2)	0.023(2)	0.004(2)

TABLE XI Bond lengths (Å) of DCB

Atom	*Atom*	*Distance*	*Atom*	*Atom*	*Distance*
Cl(11)	N(10)	1.723(4)	Cl(12)	N(10)	1.733(4)
S(7)	O(8)	1.415(3)	S(7)	O(9)	1.419(3)
S(7)	N(10)	1.741(4)	S(7)	C(6)	1.741(3)
C(1)	C(2)	1.371(5)	C(1)	C(6)	1.375(5)
C(2)	C(3)	1.374(6)	C(3)	C(4)	1.375(6)
C(4)	C(5)	1.372(5)	C(5)	C(6)	1.392(5)

TABLE XII Bond angles (°) of DCB

Atom	*Atom*	*Atom*	*Angle*	*Atom*	*Atom*	*Atom*	*Angle*
O(8)	S(7)	O(9)	120.9(2)	O(8)	S(7)	N(10)	102.6(2)
O(8)	S(7)	C(6)	111.0(2)	O(9)	S(7)	N(10)	102.8(2)
O(9)	S(7)	C(6)	110.4(2)	N(10)	S(7)	C(6)	107.7(2)
Cl(11)	N(10)	Cl(12)	109.9(2)	Cl(11)	N(10)	S(7)	110.6(2)
Cl(12)	N(10)	S(7)	109.9(2)	C(2)	C(1)	C(6)	118.9(4)
Cl(1)	C(2)	C(3)	120.2(4)	C(2)	C(3)	C(4)	120.6(4)
C(3)	C(4)	C(5)	120.4(4)	C(4)	C(5)	C(6)	118.2(4)
S(7)	C(6)	C(1)	119.1(3)	S(7)	C(6)	C(5)	119.2(3)
C(1)	C(6)	C(5)	121.6(3)				

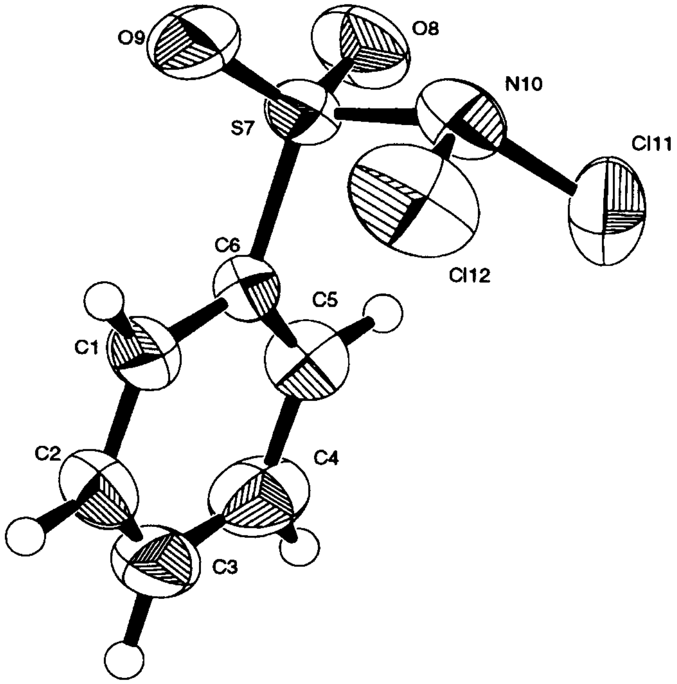


FIGURE 7 ORTEP diagram of DCB.

DBB. The N—Cl distance of 1.729(1) Å equals the mean N—Cl distance in $NCl_3(S)$ and is the same as one of the distances in $[PtCl(NH_3)_3(NCl_2)_2]$ Cl (1.75(2) 1.66(1) Å). S(7)—O8 and S(7)—O9 distances of 1.415(1) and 1.419(1) Å, agree well with the reported structure of similar molecules [2]. There is no observable change in the C—C bond (1.372(1) Å) of the phenyl ring. We can observe the hydrogen bonding in the following schemes: C5—H8 = 2.628(1)Å, C5—H...Cl11 = 3.156(2) Å), Cl—H...O9 = 2.589(1) Å Cl—H...Cl12 = 3.144(1)Å.

Crystal Structure of DCT

The colorless crystals of DCT are readily obtained by slow evaporation using CCl_4. A colorless rectangular crystal of dimension 0.2 × 0.2 × 0.15 mm was selected for X-ray data collection. All measurements were made on a Rigaku AFC7S diffractometer with graphite monochromated (Mo$K\alpha$) radiation. The data were collected at a temperature of 293 K using the ω-2θ scan technique. Least-squares refinement of 25 reflections in the range $13.82 < 2\theta < 17.91°$ yielded a primitive monoclinic cell with dimensions

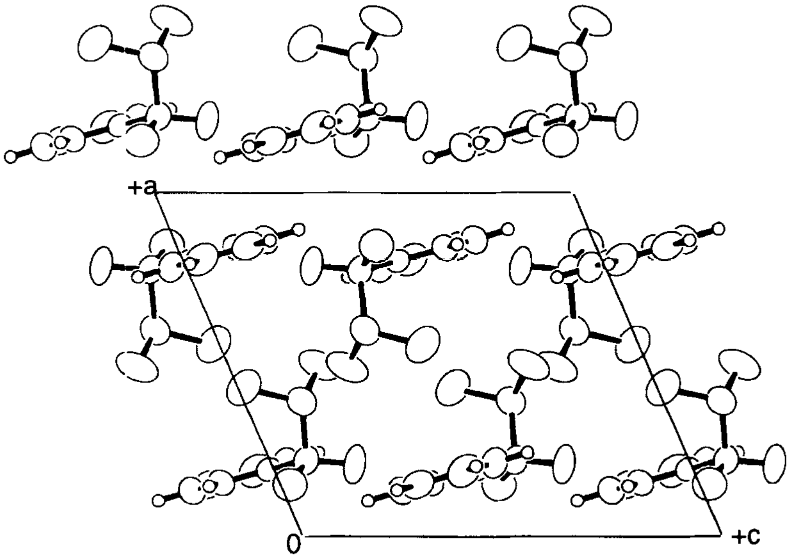


FIGURE 8 Packing of molecules down *b*-axis (DCB).

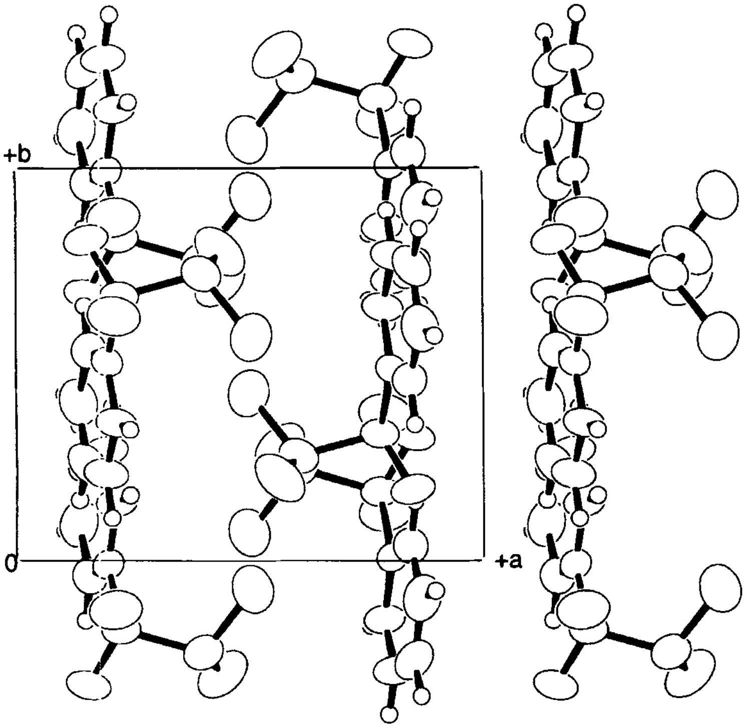


FIGURE 9 Packing of molecules down *c*-axis (DCB).

$a = 7.179(3)$ Å, $b = 16.217(2)$ Å, $c = 8.692(3)$ Å, $\beta = 96.69(3)°$, $V = 1005.1(4)$ Å^3, $Z = 4$, $F.W = 240.10$, $D_{calc} = 1.598$ gm cm^{-3}, $F_{000} = 488$, Space group $P2_1/n$ and $\mu(\text{Mo}K\alpha) = 8.2\,\text{cm}^{-1}$. In the course of data collection the intensity of the standard reflections decreased by 42.3%. A linear correction factor was applied to the data to account for this phenomenon.

An empirical absorption correction [45] based on azimuthal scans of three reflections were applied which resulted the transmission factors ranging from 0.86 to 1.00. The data were corrected for Lorentz and polarization effect (secondary extinction = 6.4794×10^{-6}). A total of 2005 data were collected in the range of $0 \leq 2\theta \leq 50$, of which 1852 were unique ($R_{int} = 0.043$). The structure was solved by direct methods (SIR92) [46] and expanded using difference Fourier maps [48]. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at chemically acceptable positions but not refined. Final full matrix least-squares cycle for 1205 reflections and 119 parameters converged to $R = 0.055$, $R_\omega = 0.079$ with goodness of fit = 2.28.

Results and Discussion

The positional parameters and equivalent temperature factors for non-hydrogen atoms are given in Table XIII. Anisotropic parameters (U_{ij}) are listed in Table XIV. Bond distances and bond angles are given in Tables XV and XVI respectively. Figure 10 represents the ORTEP diagram of the DCT molecule at 50% probability. Packing of the molecules down c-axis is shown

TABLE XIII Atom coordinates and B_{iso}/B_{eq} of DCT

Atom	x	y	z	B_{eq}
Cl(12)	0.0122(3)	0.11373(9)	0.5449(2)	9.23(5)
Cl(13)	−0.0134(2)	0.24599(8)	0.3331(2)	7.44(4)
S(8)	0.3427(2)	0.17522(7)	0.4268(1)	6.05(3)
O(9)	0.4319(6)	0.1341(2)	0.5594(4)	9.4(1)
O(10)	0.4082(6)	0.2530(2)	0.3789(5)	8.2(1)
N(11)	0.1268(7)	0.2005(2)	0.4846(4)	6.3(1)
C(1)	0.3108(6)	0.0230(2)	0.2957(5)	5.00(10)
C(2)	0.2848(6)	−0.0291(3)	0.1712(5)	5.0(1)
C(3)	0.2518(5)	0.0006(2)	0.0213(5)	4.34(9)
C(4)	0.2259(6)	−0.0572(3)	−0.1148(5)	5.8(1)
C(5)	0.2459(6)	−0.0856(3)	−0.0024(5)	4.81(10)
C(6)	0.2722(6)	0.1395(2)	0.1210(5)	4.65(9)
C(7)	0.3059(5)	0.1078(2)	0.2697(5)	4.37(9)

TABLE XIV Anisotropic displacement parameters (Å^2) for non-hydrogen atoms of DCT

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(12)	0.196(2)	0.086(1)	0.0750(9)	−0.022(1)	0.044(1)	0.0043(7)
Cl(13)	0.135(1)	0.0764(9)	0.0690(8)	0.0408(8)	0.0043(7)	−0.0090(6)
S(8)	0.106(1)	0.0520(7)	0.0630(7)	−0.0037(6)	−0.0263(6)	−0.0098(5)
O(9)	0.168(4)	0.087(3)	0.079(2)	0.017(2)	−0.073(2)	−0.010(2)
O(10)	0.138(3)	0.064(2)	0.104(3)	−0.039(2)	−0.007(2)	−0.018(2)
N(11)	0.140(4)	0.048(2)	0.050(2)	0.001(2)	0.005(2)	−0.004(2)
C(1)	0.080(3)	0.047(2)	0.059(2)	0.008(2)	−0.010(2)	0.003(2)
C(2)	0.069(3)	0.043(2)	0.076(3)	0.007(2)	−0.004(2)	−0.005(2)
C(3)	0.043(2)	0.056(2)	0.065(3)	−0.003(2)	0.005(2)	−0.016(2)
C(4)	0.071(3)	0.072(3)	0.076(3)	−0.005(2)	0.008(2)	−0.027(2)
C(5)	0.075(3)	0.057(2)	0.051(2)	−0.007(2)	0.009(2)	−0.002(2)
C(6)	0.075(3)	0.045(2)	0.056(2)	−0.004(2)	0.003(2)	0.003(2)
C(7)	0.063(2)	0.044(2)	0.056(2)	−0.001(2)	−0.007(2)	−0.004(2)

TABLE XV Bond lengths (Å) of DCT

Atom	*Atom*	*Distance*	*Atom*	*Atom*	*Distance*
Cl(12)	N(11)	1.741(4)	Cl(13)	N(11)	1.727(4)
S(8)	O(9)	1.418(3)	S(8)	O(10)	1.425(4)
S(8)	N(11)	1.733(5)	S(8)	C(7)	1.745(4)
C(1)	C(2)	1.368(6)	C(1)	C(7)	1.394(6)
C(2)	C(3)	1.383(6)	C(3)	C(4)	1.505(5)
C(3)	C(5)	1.395(6)	C(5)	C(6)	1.379(6)
C(6)	C(7)	1.386(6)			

TABLE XVI Bond angles (°) of DCT

Atom	*Atom*	*Atom*	*Angle*	*Atom*	*Atom*	*Atom*	*Angle*
O(9)	S(8)	O(10)	121.4(3)	O(9)	S(8)	N(11)	102.1(3)
O(9)	S(8)	C(7)	110.7(2)	O(10)	S(8)	N(11)	102.3(2)
O(10)	S(8)	C(7)	110.6(2)	N(11)	S(8)	C(7)	108.4(2)
Cl(12)	N(11)	Cl(13)	108.7(2)	Cl(12)	N(11)	S(8)	111.5(2)
Cl(13)	N(11)	S(8)	110.0(2)	C(2)	C(1)	C(7)	118.8(4)
C(1)	C(2)	C(3)	121.6(4)	C(2)	C(3)	C(4)	121.1(4)
C(2)	C(3)	C(5)	118.8(4)	C(4)	C(3)	C(5)	120.1(4)
C(3)	C(5)	C(6)	120.8(4)	C(5)	C(6)	C(7)	118.9(4)
S(8)	C(7)	C(1)	119.5(3)	S(8)	C(7)	C(6)	119.4(3)
C(1)	C(7)	C(6)	121.0(4)				

in Figure 11. Stacking of molecules can be observed along *a*-axis. Here also the N—Cl distance of 1.734(1) Å is same as observed in DCB. The distances S8—O10 (1.425 Å) and S8—O9 (1.428 Å) are comparable with the values found in the structures reported earlier [2]. The toluene group is quite normal with mean ring C—C bonds of 1.382(1) Å and an average deviation of 0.009Å. Hydrogen bonding in the following schemes are observed: C1—H...O9 = 2.611(1)Å, C1—H...Cl12 = 3.282(1)Å, C6—H...O10 = 2.643(1)Å, C6—H...Cl13 = 3.08(1)Å, O9—

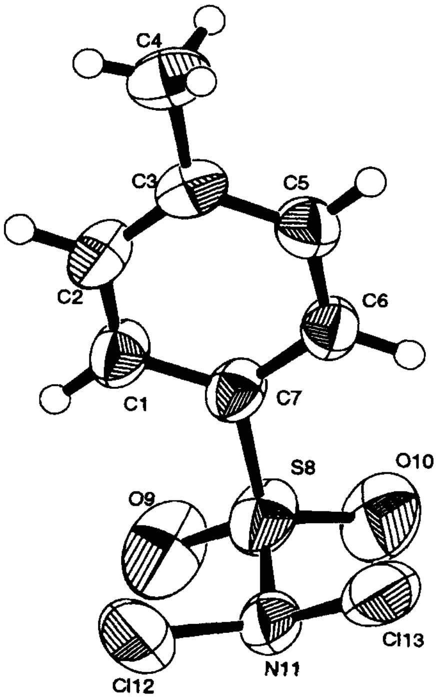


FIGURE 10 ORTEP diagram of DCT.

Cl12 = 3.019(1) Å Cl13—O10 = 3.009(1) Å. S8—N11 = 1.753(2) and S8—C7 = 1.745(1) Å.

Preparation of BAB: BAB was prepared [43] by the partial debromination of dibromamine-B, which in turn was prepared by the bromination of chloramine-B (Aldrich). Pale yellow crystals of BAB were obtained by recrystallization using methanol (available bromine content: found, 28.0%; theoretical, 28.04%).

Preparation of DBB: DBB was prepared [4] by the bromination of chloramine-B (Aldrich). Orange red crystals of DBB were obtained by recrystallization using CCl_4 (available bromine content: found, 50.70%; theoretical, 50.74%).

Preparation of DCB: DCB was prepared [31] by the chlorination of aqueous chloramine-B (Aldrich). Pale yellow crystals of DCB were obtained by recrystallization using CCl_4 (availbale chlorine content: found, 31.2% theoretical, 31.4%).

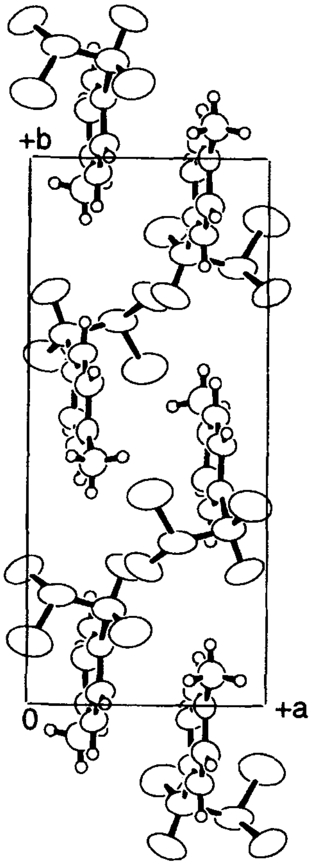


FIGURE 11 Packing of molecules down *c*-axis (DCT).

Preparation of DCT:

DCT was prepared [44] by the chlorination of aqueous chloramine-T (Aldrich). Colourless crystals of DCT were obtained by recrystallization from CCl_4 (available chlorine content: found, 29.2%; theoretical, 29.6%).

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