Spectroscopic Studies on the Reaction of Iodine with the Mixed Oxygen-nitrogen Cyclic Base 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane

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The interaction of the mixed oxygen-nitrogen cyclic base, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8] hexacosane (HOD-ABCHC) with iodine as a σ-acceptor has been studied spectrophotometrically at room temperature in CHCl₃. The spectra indicate the formation of the triiodide ion, I_3^- and the complex was formulated as $[(HODABCHC)I]^+ \cdot I_3^-$ in good agreement with elemental analysis, photometric titration plots based on the characteristic absorption bands of I_3^- ion around 292 and 360 nm and infrared measurements. Far infrared spectrum shows the characteristic bands for I_3^- ion at 154, 105 and 56 cm^{-1} are assigned for the v_s(I-I), v_s(I-I) and $\delta(I_3^-)$, respectively.

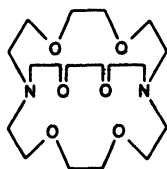**Key Words: 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8,8,8] hexacosane, Iodine, Spectra.**

INTRODUCTION

It has been well established that the rapid development in the field of electron donor-acceptor interaction arose from the electronic absorption study on iodine complexes by Benesi and Hildebrand[1], and the theoretical interpertation of the spectra by Mulliken[2]. Nour *et al*[3–6] reported the formation of the polyiodide ions, I_n^- (n = 3, 5, 7 and 9) in the reaction of iodine with various bases containing nitrogen, oxygen and sulphur donor atoms. The formed charge transfer complexes were formulated as $[(base)I]^+ \cdot I_n^-$.

However, the formation of charged transfer (CT) complexes depends strongly on the type and nature of the donor base as well as the electron acceptors[7]. The variation of the spectrophotometric properties of the CT-complexes in different solvent with different polarities are assumed to be due to the solvent interactions with the electron acceptors[8, 9].

In the present study, the synthesis and spectroscopic studies of the iodine complex formed in the reaction of iodine with mixed oxygen-nitrogen cyclic base 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8] hexa-cosane (HODABCHC) (I) is repoted. The obtained results enable us to investigate the nature of the formed complex. The study of the CT-complexes is of special interest due to their important physical properties such as electrical conductivities[10].

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(I)
4,7,13,16,21,24-hehaoxa-1,10-
diazabicyclo-[8,8,8]hexacosane
(HODABCHC)
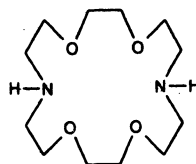
(II)
1,4,10,13-tetraoxa-7,16-
diazacyclooctadecane
(TODACOD)

EXPERIMENTAL

All chemicals used were of high grade quality. The mixed oxygen-nitrogen cyclic base 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8,8,8]hexacosane (HODABCHC) was obtained from Merk, while R.G. quality iodine (Hayashi Pure Chemical Indust. Ltd.) was used.

The solid base-iodine complex, $[(HODABCHC)I]^+ \cdot I_3^-$ was isolated as a dark brown solid by the addition of excess saturated iodine solution in chloroform (40 mL) to a saturated solution (10 mL) of the (HODABCHC) base in chloroform. The dark brown precipitate was filtered off, washed several times with minimum amounts of chloroform and dried under vacuum. The formed iodine complex was characterized by spectroscopic data as well as elemental analysis as $[(HODABCHC)I]^+ \cdot I_n^-$. Anal. Found (Calcd.) (%) : C, 23.7 (24.0); H, 3.8 (4.0%); N, 2.7 (3.0) and I, 56.5 (57.3).

The electronic absorption spectra of iodine, base (HODABCHC) and the formed $[(HODABCHC)I]^+ \cdot I_n^-$ complex in chloroform were recorded in the region of 700–250 nm using UV-Vis spectrophotometer model JASCO V-530 with quartz cell of 1.0 cm path length. The mid infrared of the donor (HODABCHC) formed complex, $[(HODABCHC)I]^+ \cdot I_n^-$, was recorded from KBr discs using Genesis-II FT-IR spectrometer, while the far infrared spectra for the same compounds were recorded from Nujol mulls dispersed on polyethylene windows in the region 300–50 cm^{-1} using Mattson infinity series FT-IR spectrometer. Photometric titration of iodine and (HODABCHC) was studied in chloroform at 25°C using an HeλIOS γ-Unicam UV-Vis spectrophotometer. The concentration of the mixed oxygen-nitrogen cyclic base was kept fixed at 1×10^{-4} M, while the concentration of iodine in the reaction mixture was varied from 0.25×10^{-4} to 4×10^{-4} M. These concentrations produce base : I_2 ratio varying from 1 : 0.25 to 1 : 4. The spectrum was then recorded for each mixture and the absorptions of the product, iodine complex, were measured around 292 and 360 nm and plotted as a function of the added X mL of iodine in order to determine the stoichiometry of the reaction according to the known photometric titration method[11].

RESULTS AND DISCUSSION

The electronic absorption spectra of iodine, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane (HODABCHC) and (HODABCHC)-I_2 mixture were recorded in chloroform (Fig. 1). The spectrum of the reaction mixture
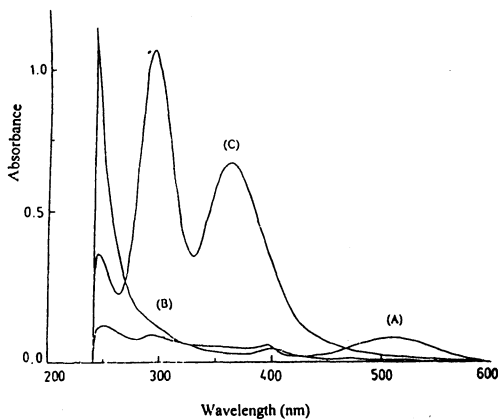

Fig. 1. Electronic absorption spectra of HODABCHC (5×10^{-6} M), iodine (5×10^{-6} M) and their mixture in $CHCl_3$: (A) iodine, (B) HODABCHC, (C) HODABCHC-I_2 mixture.

exhibits two strong absorption bands around 292 and 360 nm which are not due to any of the reactants. Photometric titration measurements were based on these two absorptions of the formed iodine complex and are plotted as shown in Fig. 2. The HODABCHC-I_2 equivalence point shown in these curves clearly indicate
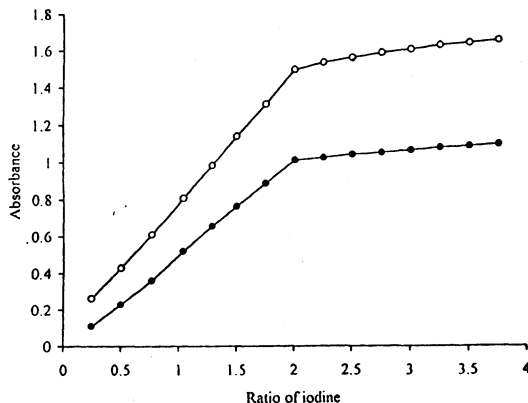

Fig. 2. Photometric titration curves for HODABCHC-I_2 in $CHCl_3$:
——O——292 nm band; ——●——360 nm band.

that the HODABCHC : I_2 ratio is 1 : 2 in agreement with the elemental analysis data of the formed solid iodine complex. On the other hand, the two absorptions of the HODABCHC-I_2 mixture occurring around 292 and 360 nm are well known[4, 12-14] to be characteristic for the formation of the triiodide ion (I_3^-). X-ray structural studies on several triiodide salts[15] indicates that the I_3^- ion could be linear or non-linear. However, the I-I bond may or may not have equal bond

lengths. Both the linear I_3^- ion, with two unequivalent bond lengths, ($C_{\alpha v}$ symmetry) and the non-linear I_3^- ion with two unequivalent bond lengths (C_s symmetry) are expected to display three infrared bands. These are $v_s(I–I)$, $v_s(I–I)$ and δ (I_3^-). The observation of these three fundamentals in the far infrared spectrum of $[(HODABCHC)I]^+ \cdot I_3^-$ at 154, 105 and 56 cm^{-1} supports the existence of I_3^- ion either with linear ($C_{\alpha v}$) or non-linear (C_s) structure (Table-1). Accordingly, the obtained iodine complex is formulated as $[(HODABCHC)I]^+ \cdot I_3^-$.

<div align="center">

TABLE-1

FUNDAMENTAL VIBRATIONS OF SOME TRIIODIDE COMPOUNDS

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Compounds	Assignments*			References
	v_1	v_2	v_3	
KI_3	111		143	15
CsI_3	103	69	149	21
$(CH_3)NI_3$	111	74	138	21, 22
$(C_2H_5)_4NI_3$	104	72, 66	132	20
$(TACPD)I^+ \cdot I_3^-$	109	60	132	5
$(HMTACTD)I^+ \cdot I_3^-$	110	61	144	5
$[(HODABCHC)I]^+ \cdot I_3^-$	105	56	154	Present work

v_1, v_s (I—I); v_2, δ (I_3^-); v_3, v_{as} (I—I)

A general mechanism is proposed for the formation of $[(HODABCHC)I]^+ \cdot I_3^-$ complex as follows:

(i) $(HODABCHC) + I_2 \rightleftharpoons [(HODABCHC)I]^+ \cdot I^-$

(ii) $[(HODABCHC)I]^+ \cdot I^- + I_2 \rightleftharpoons [(HODABCHC)I]^+ \cdot I_3^-$

The formation of the iodide intermediate $[(HODABCHC)I]^+ \cdot I^-$ is well known to be formed between iodine and cyclic polyamines[5, 6].

The infrared spectra of the $[(HODABCHC)I]^+ \cdot I_3^-$ complex and the free base (HODABCHC) were recorded (Fig. 3). Table-2 shows the observed frequencies and their assignments. However, the recorded spectrum of $[(HODABCHC)I]^+ \cdot I_3^-$ complex is quite similar to the infrared of the free base, but with some changes in its band intensities and shifts of some band frequency values. The infrared band intensities of the free base (HODABCHC) are relatively higher than those associated with the infrared bands of the iodine complex. This means that the symmetry of the (HODABCHC) is increased upon complexation with iodine implying a smaller change in the dipole moment during the base vibration in the complex form and hence it shows a relatively weaker band intensities. However, the shift to higher frequency values of $v(C—N)$ and $v(C—O)$ bond vibrations in the spectrum of the base upon complexation to iodine (Table-2) could be due to the increase of force constant values of both the C—O and C—N bonds. Such an increase is associated with the expected reduce of electron repulsion between these bonded atoms as a result of the donation from both the N and O electron pairs to iodine. On the other hand, the $v(I—I)$ bond
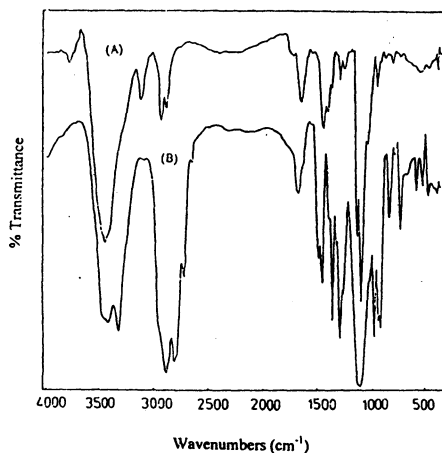
Fig. 3   Infrared spectra of (A) [(HODABCHC)I]$^{+}$·I$_3^-$ complex and (B) free base (HODABCHC).

TABLE-2

CHARACTERISTIC INFRARED FREQUENCIES (cm^{-1}) AND TENTATIVE
ASSIGNMENTS FOR [(HODABCHC)] AND [(HODABCHC)I]$^{+}$·I$_3^-$ COMPLEX

(HODABCHC)	(CHODABCHC)I]$^{+}$·I$_3^-$	Assignments
3457 vs	3433 vs	ν(O—H); H$_2$O of KBr
3317 vs	3320 m	ν(C—H); —CH—, —(CH$_2$)—
2877 vs	2906 m	and —(CH$_2$)$_2$
2804 vs	2867 m	
2716 s	2722 sh	
1640 ms	1639 m	δ(H$_2$O); KBr
1479 s	1483 ms	C—H deformation; —(CH)—,
1446 s	1432 m	—(CH$_2$)— and —(CH$_2$)—
1460 s	1458 w	
1357 s	1395 w	ν(C—C), ν(C—N), ν(C—O)
1290 s	1310 w	
	1287 s	
1111 vs	1132 vs	
995 s	1000 m	(C—H) bend; —CH—,
919 s	925 w	—(CH$_2$)— and —(CH$_2$)$_2$—
836 s	830 vw	
792 m	778 w	Skeletal vibration CH in-plane
728 m	710 vw	bend, (C—O—C)
674 m	650 vw	
575 m	561 vw	CH out of plane bend, skeletal
522 m	515 vw	vibration
464 m	467 vw	

s = strong, w = weak, m = medium, sh = shoulder and v = very

vibrations of the triiodide ion moved to lower frequency values at 105 and 154 cm^{-1} (Table-1) compared to that of free iodine at 180 cm^{-1}.[16] As iodine becomes coordinated to a donor, the force constant is reduced and ν(I—I) bond vibration moves to lower frequency value. This is a consequence of the donation of electron density into the σ^{*}-antibonding orbital of iodine. Gabes and Elst[17] have indicated that the I—I bonds in the triiodide ion are weak compared to the bond in the free iodine with the corresponding I—I stretching force constant values of 0.90 and 1.72 mdyn/Å, respectively.

Finally, it is of interest to indicate here that the iodine complex reported in this study, $[(HODABCHC)I]^{+} \cdot I_3^{-}$, formed between the base 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane and iodine, with the base : I_2 ratio of 1 : 2 is different from that previously reported[5], $[(TODACOD)I]^{+} \cdot I_5^{-}$ in the reaction of iodine with the related mixed oxygen-nitrogen cyclic base, 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (TODACOD) where the (TODACOD) : I_2 ratio is 1 : 3. The lower value of (HODABCHC) : I_2 ratio, (1 : 2), is clearly related to that the cavity of (HODABCHC) molecule shown in (I) is smaller compared with that in (TODACOD) molecule shown in (II) implying a relatively higher steric hindrance in (HODABCHC) forming a smaller size polyiodide ion, I_3^{-} rather than I_5^{-}.

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