Synthesis and spectroscopic characterization on the tri-iodide charge transfer complex resulted from the interaction between morpholine as donor and iodine σ-acceptor

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Abstract
Charge-transfer (CT) complex formed between morpholine (Morp) as donor with iodine (I\(_2\)) as acceptor has been studied spectrophotometrically. The synthesis and characterization of morpholine CT-complex of iodine, \([\text{Morp}][\text{I}^+ \cdot \text{I}^-]_2\) was described. This complex is readily prepared from the reaction of Morp with I\(_2\) within CHCl\(_3\) solvent. IR spectra, UV–Vis techniques and elemental analyses (C, H and N), characterize the Morph charge-transfer complex. Benesi–Hildebrand and its modification methods were applied to the determination of association constant (K), molar extinction coefficient (\(e\)).

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1. Introduction

Morpholine (Morp) is an organic chemical compound having the chemical formula O(CH₂CH₂)₂NH (Formula I). Morpholine is a common additive, in ppm concentrations, for pH adjustment in both fossil fuel and nuclear power plant steam systems. Morpholine is widely used in organic synthesis. For example, it is a building block in the preparation of the antibiotic linezolid and the anticancer agent.

Table 1  Elemental analysis CHN and physical parameters data of the CT-complex formed in the reaction of the Morp with iodine.

<table>
<thead>
<tr>
<th>Complexes (FW)</th>
<th>Molecular weight</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>Physical data</th>
</tr>
</thead>
<tbody>
<tr>
<td>($[\text{Morp}]_2I^+ \cdot I^-$ (C₈H₁₈N₂O₂I₄)</td>
<td>682.00</td>
<td>13.98</td>
<td>14.10</td>
<td>2.56</td>
<td>2.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found</td>
<td>Calc.</td>
<td>Found</td>
<td>Calc.</td>
</tr>
</tbody>
</table>

Figure 1  Electronic absorption spectra of; (A) Morp–iodine reaction in CCl₄, (B) Morp–iodine reaction in CHCl₃, (C) Morp–iodine reaction in CH₂Cl₂ and (D) Morp–iodine reaction in 1,2-dichloroethane. (a) = donor (1.0 × 10⁻⁴ M), (b) = acceptor (1.0 × 10⁻² M) and (c) = CT-complex.
Figure 2   Photometric titration curves for the Morp–iodine system in various solvents; (A) in CCl₄ at 261 and 390 nm, (B) in CHCl₃ at 264 and 386 nm, (C) in CH₂Cl₂ at 272 nm and 365 nm and (D) in 1,2-dichloroethane at 277 nm and 367 nm.

Figure 3   The plot of \((C_0^+ + C_0^-)\) values against \((C_0^+ C_0^-)/A\) values for the Morp–iodine system in various solvents; (A) in CCl₄ at 390 nm, (B) in CHCl₃ at 386 nm, (C) in CH₂Cl₂ at 365 nm and (D) in 1,2-dichloroethane at 367 nm.
### Table 2  Spectrophotometric results of the Morp complex with iodine in different solvents at 25 °C and the dielectric constant of the solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>λ_max (nm)</th>
<th>E_{CT} (eV)</th>
<th>K (l mol(^{-1}))</th>
<th>(\epsilon_{max}) (l mol(^{-1}) cm(^{-1}))</th>
<th>(f)</th>
<th>(\mu)</th>
<th>(I_p)</th>
<th>(D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl(_4)</td>
<td>390</td>
<td>3.18</td>
<td>2.36 \times 10^4</td>
<td>1.18 \times 10^4</td>
<td>5.79</td>
<td>21.90</td>
<td>7.75</td>
<td>2.2</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>386</td>
<td>3.22</td>
<td>2.62 \times 10^4</td>
<td>1.08 \times 10^4</td>
<td>7.29</td>
<td>24.50</td>
<td>7.80</td>
<td>4.7</td>
</tr>
<tr>
<td>CH(_2)Cl(_2)</td>
<td>365</td>
<td>3.40</td>
<td>4.23 \times 10^4</td>
<td>3.94 \times 10^4</td>
<td>23.60</td>
<td>42.80</td>
<td>8.08</td>
<td>8.9</td>
</tr>
<tr>
<td>(CH(_2))(_2)Cl(_2)</td>
<td>367</td>
<td>3.38</td>
<td>5.17 \times 10^4</td>
<td>5.14 \times 10^4</td>
<td>30.80</td>
<td>49.00</td>
<td>8.05</td>
<td>10.4</td>
</tr>
</tbody>
</table>

Some of charge-transfer complexes show very interesting applications in the field of analytical chemistry (Bebawy and El-Kelani, 1997; Luo, 1995). Poliodide charge-transfer complexes are of special interest and importance. This is because some of these complexes have shown interesting properties such as electrical conductivity. The highly conducting complex \([(\text{TTS})_2]\text{I}^+ \cdot \text{I}_3\) is reported (Trotter and White, 1978) to be formed in the reaction of iodine with the sulphur containing base tetrathiotetracene (TTS).

In previous studies (Mizuno et al., 1981; Nour et al., 1986a,b; Mulazzi et al., 1981; Nour, 2000; Nour and Shahada, 1988), it has been stated that iodine reacts with bases like cyclic polyamines, polysulphur and mixed oxygen–nitrogen to form stable charge-transfer complexes with the formation of poliodide ions \(\text{I}_n^+\) (\(n = 3, 5, 7\) and 9).

In continuity with our interest in the study of interaction of charge-transfer (CT) complexes Teleb, 2004; Refat et al., 2004, 2005, 2006a,b, 2007; Refat, 2005, the present article includes the characterization of charge-transfer complexes of Morp with iodine as acceptor. Association constants \((K)\), molar extinction coefficient \((\epsilon)\), oscillator strength \((f)\) are evaluated. The solid complex was synthesized and studied by elemental analysis (CHN), infrared and electronic spectra.

2. Materials and methods

All chemicals used throughout this work were Analar or extra pure grade. Morpholine, O(CH\(_2\)CH\(_2\))\(_2\)NH, was of analytical reagent grade (Merck reagent). Iodine as a \(\sigma\)-acceptor was purchased from Aldrich. Stock solutions of morpholine or iodine as acceptor were freshly prepared and the spectroscopic grade chloroform (Merck Co.) was used as received.

3. [Morphiline–iodine complex]

The morphiline–iodine CT-complex with the general formula \([(\text{Morp})_2]\text{I}^+ \cdot \text{I}_3\), was isolated as a dark brown solid by the mixing (87.12 mg, 1.0 mmol) of the donor in chloroform (10 ml), a solution of iodine was added (253.81 mg, 1.0 mmol) in the same solvent (10 ml) with continuously stirring for about 15 min at room temperature and the solution was allowed to evaporate slowly at room temperature. A yellow crystal was formed, washed several times with little amounts of chloroform, and dried under vacuum over anhydrous calcium chloride; the empirical formula of the complex \([(\text{Morp})_2]\text{I}^+ \cdot \text{I}_3\) is \(\text{C}_8\text{H}_{18}\text{N}_2\text{O}_2\text{I}_4\) with molecular weight 682.00 g/mol.

4. Instrumentation and physical measurements

The Electronic spectra of the donors, iodine and the resulted CT-complex were recorded in the region of 200–800 nm by using a Jenway 6405 Spectrophotometer with quartz cells, 1.0 cm path in length. Photometric titration was performed at 25 °C for the reactions of Morp donor with iodine acceptor in chloroform, as follows: the concentration of the donor in the reaction mixtures was kept fixed at 5.0 \times 10^{-4} M, while the concentration of iodine was changed over a wide range from \(X \times 10^{-4}\) to \(Y \times 10^{-4}\) M. These produced solutions with donor:acceptor molar ratios varying from 1:0.25 to 1:4.00.

IR measurements (KBr discs) of the solid donors, acceptor and CT-complexes were carried out on a Bruker FT-IR spectrophotometer (400–4000 cm\(^{-1}\)).

5. Results and discussion

The elemental analysis data (C, H and N) of the Morp charge transfer complex were performances and listed in Table 1. From this table, it can be seen that the resulted values are agree quite well with the calculated values, and the suggested of the CT-complex is matched with the molar ratios introduced from the photometric titration curves. The entire Morp CT-complex is insoluble in cold and hot water, but easily soluble in DMF and DMSO.

6. Electronic absorption spectra of Morp/iodine system

The UV–Vis absorption spectra of the iodine complex were measured in various solvents such as CCl\(_4\), CHCl\(_3\), CH\(_2\)Cl\(_2\) and 1,2-dichloroethane. In each solvent the complex is formed by adding \(X\) ml of \(5.0 \times 10^{-4}\) M (iodine) (\(X = 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50\) and \(3.00\) ml) to \(1.00\) ml of \(5.0 \times 10^{-4}\) M morpholine. The volume of the mixture in each case was completed to \(10\) ml for (CCl\(_4\)), 10 ml for (CHCl\(_3\)), 20 ml for (CH\(_2\)Cl\(_2\)) and 20 ml for (1,2-dichloroethane) with the respected

![Figure 4](image-url)  
**Figure 4** The plot of the oscillator strength \(f\) of \([(\text{Morp})_2]\text{I}^+ \cdot \text{I}_3\) against the dielectric constant of the solvent \(D\).
solvent. The concentration of Morp in the reaction mixture was kept fixed at $0.50 \times 10^{-4}$, $0.50 \times 10^{-4}$, $0.25 \times 10^{-4}$ and $0.25 \times 10^{-4}$ M in the case of using CCl$_4$, CHCl$_3$, CH$_2$Cl$_2$ and 1,2-dichloroethane solvents, respectively. While the concentration of iodine was varied over the range of $0.125 \times 10^{-4}$ M to $1.50 \times 10^{-4}$ M for Morp/I$_2$ system in CCl$_4$ solvent, from $0.125 \times 10^{-4}$ M to $1.500 \times 10^{-4}$ M for Morp/I$_2$ system in CHCl$_3$ solvent, from $0.0625 \times 10^{-4}$ M to $0.7500 \times 10^{-4}$ M for Morp/I$_2$ system in CH$_2$Cl$_2$ and from $0.0625 \times 10^{-4}$ M to $0.7500 \times 10^{-4}$ M for Morp/I$_2$ system in 1,2-dichloroethane solvent, respectively. These concentrations produce Morp: I$_2$ ratios extending along the range from 1:0.25 to 1:3.00. The electronic absorption spectra of the 1:1 ratio in CCl$_4$, CHCl$_3$, CH$_2$Cl$_2$ and 1,2-dichloroethane together with the reactants I$_2$ and Morp are shown in Fig. 1A–D, respectively.

The spectra show characteristic real absorption bands which are not present in the spectra of the reactants free iodine and Morp. These bands are assigned at (390 and 261 nm), (386 and 264 nm), (365 and 272 nm) and at (367 and 277 nm) due to the CT-complex formed in the reaction mixtures of Morp with I$_2$ in the solvents CCl$_4$, CHCl$_3$, CH$_2$Cl$_2$ and 1,2-dichloroethane, respectively. Photometric titration curves based on these characterized absorption bands are given in Fig. 2A–D.

These photometric titration curves were obtained according to the known methods (Skoog, 1985) by the plot of the absorbance against the X ml added of the iodine σ-acceptor. The equivalence points shown in these curves clearly indicate that the formed CT-complex between Morp and iodine is 1:1. The formation of 1:1 complex was strongly supported by elemental analysis, mid and far infrared spectra.

However, the appearance of the two absorption bands around $\approx$360 and $\approx$270 nm are well known (Kiefer and Bernstein, 1972; Andrews et al., 1980; Kaya et al., 1972), to be characteristic for the formation of the tri-iodide ion (I$_3^-$).

Figure 5  Infrared spectra of: (A) Morp and (B) The charge-transfer complex, [(Morp)$_2$I$^+$ · I$_3^-$].
Accordingly, the formed complex was formulated as 
\[ ([\text{Morp}]_2)^+ \cdot I_2. \]

It was of interest to observe that the solvent has an effect on the spectral intensities of the formed \([([\text{Morp}]_2)^+ \cdot I_2\) complex. To study the solvent effect in a quantitative manner, it was necessary to calculate the values of the equilibrium constant, \(K\), the extinction coefficient \(\epsilon\) and the oscillator strength, \(f\), of the iodine complex in each solvent. The 1:1 modified Benson-Hildebrand equation (Abu-Eittah and Al-Sugeir, 1976) was used in the calculations.

Where \(C_a^o\) and \(C_t^o\) are the initial concentrations of the acceptor (I₂) and the donor Morp, respectively, and \(A\) is the absorbance of the detected bands around 270 and 360 nm. When the \(C_a^o - C_t^o\)/\(A\) values for each solvent are plotted against the corresponding \((C_a^o + C_t^o)/2\) values. Straight lines are obtained with a slope of \(1/K\) and intercept of \(1/kE\) as shown in Fig. 3A–D for the reaction mixtures in CC1₄, CHCl₃, CH₃Cl and 1,2-dichloroethane. The oscillator strength \(f\) was obtained from the approximate equation (Tsuhomura and Lang, 1964). Where \(v_{1/2}\) is the band-width for half-intensity in \(cm^{-1}\). The oscillator strength \(f\) values together with the corresponding dielectric constant \((\varepsilon)\) of the solvent used are given in Table 2. The trend of the values in this table reveals several facts. (i) The \([([\text{Morp}]_2)^+ \cdot I_2\) shows high values of both the equilibrium constant \((K)\) and extinction coefficient \((\epsilon)\). This high value of \((K)\) reflects the high stability of the iodine complex as a result of the expected high donation of the Morp, while the high value of \((\epsilon)\) agrees quite well with the existence of tri-iodide ion, \(I_3^-\), which is known to have high absorptivity value (Kiefer and Bernstein, 1972; Andrews et al., 1980; Kaya et al., 1972). (ii) The values of the oscillator strength, \(f\), increases with increasing in the dielectric constant \((D)\) of the solvent. This result could be explained on the basis of competitive solvent interactions with the acceptor (Ayad, 1994). Fig. 4 shows the obtained linear relationship between \(f\) and \(D\). (iii) The formation constant \((K)\) for the \([([\text{Morp}]_2)^+ \cdot I_2\) shows some variation, Table 2, as the solvent is changed, but no clear relation with solvent properties can be obtained.

Finally, the general mechanism for the formation of \([([\text{Morp}]_2)^+ \cdot I_2\) complex is proposed as follows:

\[ 2\text{Morp} + I_2 \rightarrow ([([\text{Morp}]_2)^+ \cdot I_2) \]
\[ [([\text{Morp}]_2)^+ \cdot I_2] + I_2 \rightarrow ([([\text{Morp}]_2)^+ \cdot I_3^-] \]

The formation of \([([\text{Morp}]_2)^+ \cdot I_2\) reaction intermediate is analogous to the well known species \([\text{donor}I]^+\) formed in the reaction of iodine with many donors (Hassan, 2004; Rabie, 2006). It has characteristic (Harada et al., 1981) absorption, around 250 nm; see Fig. 3A–D. The transition dipole moment \((\mu)\) of the iodine complex, Table 2, have been calculated from the equation (Rathone et al., 1997). The ionization potential \((I_p)\) of the free donor was determined from the CT energies of the CT band of its complexes with iodine by using the following equation (Aloisi and Pignataro, 1973; Foster, 1969; Kinoshita, 1962):

\[ I_p(eV) = 2.90 + 1.89 \times 10^{-4} \nu(cm^{-1}) \]

where \(E_{CT}\) is the energy of the charge-transfer of the iodine complex, the energy of the \(\pi-\sigma^*/\pi-\sigma^*\) interaction \((E_{CT})\) is calculated using the following equation (Briegleb, 1960a,b).

7. Infrared spectra of the Morp–iodine solid complex

The mid infrared spectra of Morp and the solid CT-complex, \([([\text{Morp}]_2)^+ \cdot I_2)\), were recorded from KBr discs. These spectra are shown in Fig. 5A and B, respectively. The spectral bands are resolved and assigned into their vibrational modes and given in Table 3. As expected, the bands characteristic for the Morp unit in \([([\text{Morp}]_2)^+ \cdot I_2\) CT-complex are shown with small changes in both band intensities and frequency values. For example, the \(\nu(N–H)\) vibration occur at 3424 and (splitting, 3418 and 3306) \(cm^{-1}\) for free Morp and

<table>
<thead>
<tr>
<th>Morp</th>
<th>([([\text{Morp}]_2)^+ \cdot I_2))</th>
<th>Assignments(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3424 s, br, 3300 w, sh</td>
<td>3418 ms, 3306 ms</td>
<td>(\nu(N–H))</td>
</tr>
<tr>
<td>2959 vs</td>
<td>3023 w</td>
<td>(\nu_d(C–H))</td>
</tr>
<tr>
<td>2839 vs</td>
<td>2977 vv</td>
<td>(\nu_d(C–H))</td>
</tr>
<tr>
<td>2753 mw, 2686 vw</td>
<td>2867 vv, 2812 w, 2771 ms, 2702 ms</td>
<td>Hydrogen bonding</td>
</tr>
<tr>
<td>1655 ms</td>
<td>1645 ms</td>
<td>(\delta_{ad}(N–H))</td>
</tr>
<tr>
<td>1561 vw</td>
<td>1552 vs</td>
<td>Ring breathing bands</td>
</tr>
<tr>
<td>1545 vw, 1521 vw, 1457 s, 1400 w</td>
<td>1449 s, 1416 s</td>
<td>C–H deformation</td>
</tr>
<tr>
<td>1351 w</td>
<td>1348 ms</td>
<td>(\nu(C–C))</td>
</tr>
<tr>
<td>1318 s</td>
<td>1301 vs</td>
<td>(\nu(C–N))</td>
</tr>
<tr>
<td>1273 w</td>
<td>1218 vs</td>
<td>(\nu(C–O–C))</td>
</tr>
<tr>
<td>1250 w, 1228 w, 1200 w, 1136 sh, 1106 vs, 1064 w, 1033 ms</td>
<td>1181 s, 1098 vs, 1038 s</td>
<td></td>
</tr>
<tr>
<td>890 vw</td>
<td>867 vs</td>
<td>(\nu(C–H)) bend</td>
</tr>
<tr>
<td>836 s</td>
<td>667 vv</td>
<td>(\delta_{rock}; \text{NH})</td>
</tr>
<tr>
<td>765 s</td>
<td>584 vs</td>
<td>CH₃ Rock</td>
</tr>
<tr>
<td>595 s</td>
<td>507 vv, 430 w</td>
<td>Skeletal vibrations</td>
</tr>
<tr>
<td>442 mw</td>
<td></td>
<td>CNC deformation</td>
</tr>
</tbody>
</table>

\(^a\) s = strong, w = weak, m = medium, sh = shoulder, v = very, br = broad.

\(^b\) \(\nu\), stretching; \(\delta\), bending.
[(Morp)$_2$I$^+$ · I$_3^-$], respectively. The decreasing in the intensity of $\delta$(N–H) vibration in case of iodine complex rather than Morp alone as well as the blue shifted in the wavenumbers from 1655 cm$^{-1}$ (Pip) to 1645 cm$^{-1}$ (iodine complex). Such these changes clearly indicate that the N–H bond in Morp donor is involved in the complexation process with iodine. On the other side, the presence of collected bands at 2771, 2702, 2624, 2580, 2511 and 2408 cm$^{-1}$ value, these could be assigned to the expected hydrogen bonding in the Morp/iodine complex (Bellamy, 1975). This fact is strongly interpretation the mode of interaction between Morp and iodine by forming hydrogen bond between donor “Morp” and “iodine” acceptor (N–H ·· I).

9. Far infrared spectra of the Morp–iodine solid complex

The far infrared spectrum of [(Morp)$_2$I$^+$ · I$_3^-$] was recorded from Nujol mulls dispersed on polyethylene windows in the

![Figure 6](image-url)
region 50–200 cm$^{-1}$ and shown in Fig. 6. The spectrum associated with the $\left[\text{Morp}_2\right]^{\pm} \cdot I_3^-$ complex shows the detected bands distinguished for the tri-iodide ion, $I_3^-$ at 158, 109 and 79 cm$^{-1}$. These bands can be attributed to the $v_{\text{as}}(I-I)$, $v_{\text{as}}(I-I)$ and $\delta(I^-)$, respectively. These three absorption bands do not exist in the spectrum of the donor, Morp. However, the $I_3^-$ ion may be linear ($D_{\infty h}$) or non-linear ($C_{2v}$). Group theoretical analysis indicates that the $I_3^-$ with $C_{2v}$ symmetry displays three vibrations $v_1(I-I)$, $A_1$, $v_2(I-I)$, $B_2$ and $\delta(I^-)$, $A_1$, all are infrared active in agreement (Kiefer and Bernstein, 1972; Maki and Forneris, 1967; Parrett and Taylor, 1970) with the observed three infrared bands for $\left[\text{Morp}_2\right]^{\pm} \cdot I_3^-$. 

References