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Interaction of Morpholine and Thiomorpholine with Molecular Diiodine: X-Ray Crystal Structure of Morpholinium Triiodide

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ABSTRACT

*The reactions between the donors morpholine (**1**) and thiomorpholine (**2**) with I_2 in low polar solvents (C_6H_6, $CHCl_3$, CH_2Cl_2) and different donor/I_2 concentration ratios (1:1, 1:2, 1:3) yield solids of stoichiometry $1\cdot I_2$, $1H^+I_3^-$, $1H^+I_5^-$, $2\cdot I_2$, and $2H^+I_3^-$. Crystals suitable for X-ray structure determination have been obtained only for $\mathbf{1}H^+I_3^-$. All the solids were characterized by FT-Raman and FT-IR spectroscopies in the region of the ν(I–I) frequencies. Studies in solution have been carried out on each of the reactions between **1**, **2**, and N-methylmorpholine (**3**) with I_2. The formation constants of the 1:1 adducts of **2** and **3** determined at 20°C by UV-visible spectroscopy are 8500 and 8400 $dm^3\ mol^{-1}$, respectively. IR spectroscopy shows that I_2 binds the nitrogen of **1** and **2** both in axial and equatorial positions. Further, FT-Raman and ^{13}C NMR spectroscopies support the nature of weak adducts between **1** (**2**) and the molecular diiodine in solution.*

INTRODUCTION

For some time, we have been interested [1] in the donor-acceptor interaction between molecular diiodine and several donors (D), all containing sulfur and selenium donor atoms, and have studied the equilibrium of the charge-transfer complex $D\cdot I_2$ formation, i.e.,

$$D + I_2 \rightleftarrows D\cdot I_2 \qquad 1$$

by UV-visible spectroscopy. This study was carried out to point out the influence of the chemical environment on the donor properties of the two chalcogens. More recently, our studies have been focused on solid products, by single-crystal X-ray diffraction studies and by FT-Raman spectroscopy. A comparison between the results obtained in solution and in the solid state has shown that very often the stoichiometries of the solids are different from those in solution, where normally 1:1 adducts are formed.

In fact, besides neutral charge-transfer complexes, $D\cdot I_2$, where diiodine binds linearly with the donor atom [2], it is possible to prepare $D\cdot nI_2$ compounds [3], in which other diiodine molecules interact with the coordinated I_2. Depending on several

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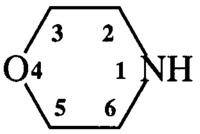
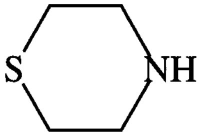
factors (nature of the donor, solvent, reagent ratio, etc.), instead of neutral adducts, ionic compounds with the oxidized donor balanced by polyiodides (I^-, I_3^-, I_5^-, I_7^-, I_8^{2-}, I_{16}^{4-}, . . .) have been isolated [4]. Moreover, iodonium salts in which an I^+ binds linearly two donor molecules (heterolytic break of the I–I bond), and hypervalent selenium compounds (containing the linear I–Se–I group) could also be obtained [4,5].

As a consequence of the great variability of the solid products obtainable by reaction (1), only X-ray diffraction is conclusive for their identification. However, when a structure determination cannot be performed, information on the solid products should be inferred by other techniques, among which Raman spectroscopy has been shown to be the most promising in identifying diiodine-containing products and has been widely applied. For this reason, we have undertaken a systematic study of diiodine-containing products characterizing them both by X-ray and FT-Raman spectroscopy [6].

The crystal structure of the recently reported morpholinium pentaiodide [7] has led us to test morpholine (**1**) and thiomorpholine (**2**) as donors toward diiodine, thus extending the investigation to donors containing nitrogen in addition to chalcogen atoms.





Here, the formation constant of reaction (1) using **2** as a donor has been determined at 20°C in CH_2Cl_2 solution. To clarify the coordination site, the formation constant has also been determined for *N*-methylmorpholine (**3**) and the data compared with those of related molecules. Moreover, solid products obtained by reacting **1** · **2** with diiodine in different solvents (benzene, chloroform, and dichloromethane) are characterized by UV-visible, ^{13}C NMR, FT-IR, and FT-Raman spectroscopies. In addition, the crystal structure of morpholinium triiodide, obtained by reacting morpholinium iodide with I_2, is reported together with some crystal data for thiomorpholinium triiodide.

EXPERIMENTAL

Morpholine (**1**), thiomorpholine (**2**), *N*-methylmorpholine (**3**), diiodine, and spectroscopic solvents (benzene, chloroform, and dichloromethane) (Aldrich) were used without further purification.

General Procedure

Morpholine-diiodine (**4**), *Thiomorpholine-diiodine* (**5**), *Thiomorpholinium-triiodide* (**7**), *and Morpholinium-pentaiodide* (**8**). Diiodine dissolved in the least amount of solvent was added to a solution of **1** (**2**) (1.5 mmol) in 10 mL of solvent. The reaction was carried out for three molar ratios of donor/I_2 (1:1; 1:2; 1:3) each in three different solvents, i.e., benzene, chloroform, and dichloromethane. Each solution was allowed to react for 1 hour at 25°C, then concentrated by evaporation, the solid filtered off, and finally washed with petroleum-ether 40–60.

Morpholinium Triiodide (**6**). This product was obtained by reacting morpholinium iodide with I_2. Morpholinium iodide was prepared by reacting (**1**) dissolved in CH_2Cl_2 with a stoichiometric amount of HI (57% in water) in ultrasonic equipment. A stoichiometric amount of diiodine dissolved in CH_2Cl_2 was allowed to react with this solution under agitation for 24 hours. The solid was washed with CH_2Cl_2 and hexane.

All elemental analyses, determined for C, H, N, S, and I, were in accordance with the proposed stoichiometries.

FT-IR and FT-Raman Spectra. The infrared spectra were recorded by use of a Bruker IFS 66 Fourier transform infrared spectrometer on polyethylene pellets in the 500–80 cm^{-1} region. Solution spectra in CH_2Cl_2 were taken in the range 3400–3250 cm^{-1} in a 0.2 cm pathway quartz cell.

FT-Raman spectra were recorded by use of a Bruker FRS 100 Fourier transform Raman spectrometer, operating with a diode-pumped Nd:YAg exciting laser emitting at a 1064 nm wavelength and having a power impinging on the sample tunable up to 350 mW. The signal was detected with an indium–gallium–arsenide detector operating at room temperature; all spectra were detected at a ± 2 cm^{-1} resolution, down to about a 50 cm^{-1} Raman shift. The spectra in CH_2Cl_2 solution were recorded on solutions contained in a 0.5 cm path length quartz cell with concentrations of **1** or **2** fixed at 2.5×10^{-2} M.

X-ray Data Collection and Structure Determination. Details of the data collection and refinement of the structure of compound **6** are reported in Table 1. A crystal of approximate dimensions 0.3 × 0.4 × 0.4 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with graphite monochromatized MoK_α radiation (0.71073 Å) on an Enraf-Nonius CAD4 computer-controlled kappa-axis diffractometer. Cell constants and an orientation

TABLE 1 Crystallographic Data

Compound	**6**
Formula	$C_4H_9I_3NO$
F.w. (amu)	467.83
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	15.890(4)
b (Å)	9.650(3)
c (Å)	15.486(3)
β (°)	114.48(2)
U (Å^3)	2161(1)
Z	8
F(000)	1656
$D_{\text{calcd.}}$ (gcm^{-3})	2.876
μ (MoK$_\alpha$) (cm^{-1})	85.4
Scan mode	$\omega - \theta$
ω-scan width (°)	$1.0 + 0.35 \tan\theta$
θ-range (°)	$3 - 25$
Octants of reciprocal space explored	$+h, +k, \pm l$
Measured reflections	4121
Unique refl. with $I > 3\sigma(I)$	2769
Final R and R_w indices[a]	0.029, 0.039
No. of variables	170
GOF[b]	1.387

[a] $R = [\Sigma(Fo - k|F_c|)/\Sigma Fo]$ $R_w = [\Sigma w(Fo - k|Fc|)^2/\Sigma wFo^2]^{1/2}$
[b] $\text{GOF} = [\Sigma w(Fo - k|Fc|)^2/(N_{\text{observations}} - N_{\text{variables}})]^{1/2}$

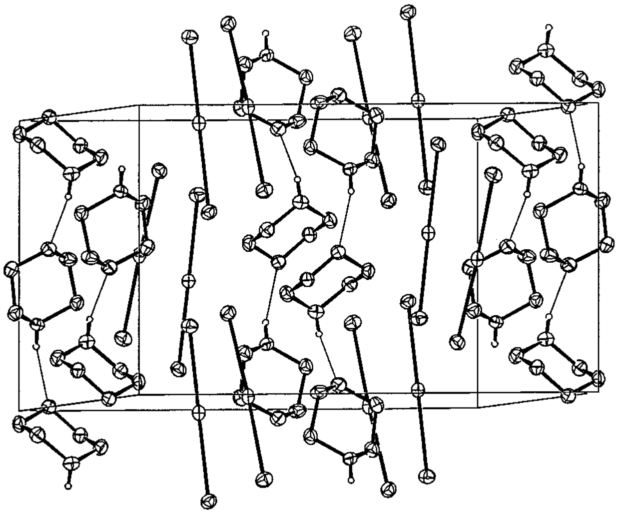


FIGURE 1. ORTEP view of the crystal packing of **6**.

TABLE 2 Stoichiometries of the Products Obtained by Reacting Morpholine **1** and Thiomorpholine **2** with Diiodine in Three Molar Ratios and Different Solvents

Solvent	*[D]/[I$_2$]*	*Products*	
Benzene	1/1 1/2 1/3	**1**·I$_2$(**4**)	2H$^+$I$_3^-$(**7**)
Chloroform	1/1 1/2 1/3	**1**·I$_2$(**4**)	**2**·I$_2$(**5**)
Dichloromethane	1/1	**1**·I$_2$(**4**)	**2**·I$_2$(**5**)
	1/2		
	1/3	**1**H$^+$I$_5^-$(**8**)	**2**H$^+$I$_3^-$(**7**)

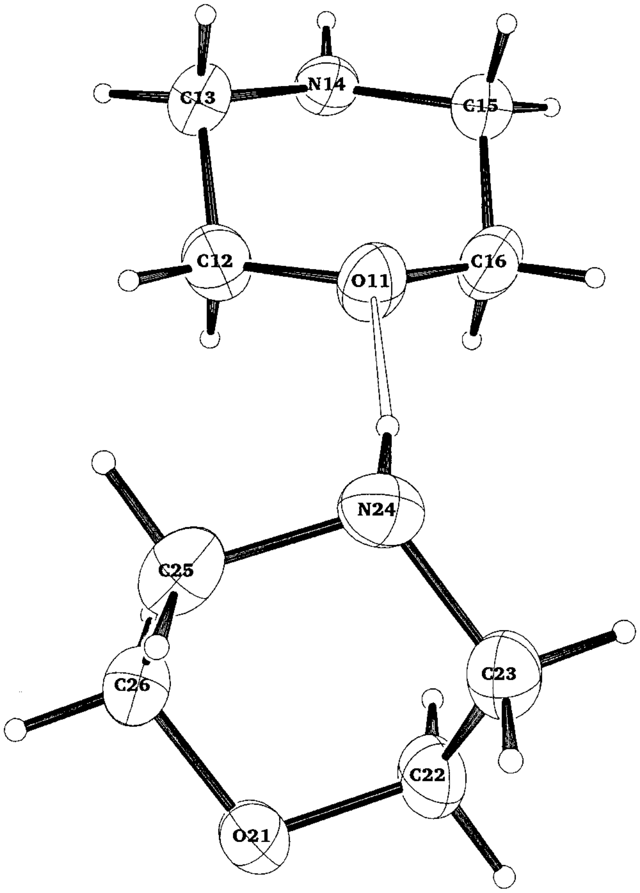


FIGURE 2. ORTEP view of two hydrogen-bonded independent cations with the atomic labeling scheme.

matrix for data collection were obtained from least-squares refinement using the setting angles of 25 reflections. The data were collected at room temperature using a variable scan rate (2°–20°/min in omega). Three representative reflections were measured every hour to check the stability of the crystal under X-ray exposure; these measurements revealed a decay of the scattering power of the crystal that amounts to about 5% of the intensity. Lorentz polarization and linear correction for decay were applied to the intensities. An empirical absorption correction, performed as described in Ref. [8], was also ap-

TABLE 3 Fractional Atomic Coordinates and Equivalent Displacement Parameters for **6**

Atom	*x*	*y*	*z*	$B_{eq}/B(\text{Å}^2)$
I(1)	−0.08548(3)	−0.05883(5)	−0.15331(3)	4.08(1)
I(2)	−0.07918(4)	−0.36422(6)	−0.17330(3)	5.03(1)
I(3)	−0.08879(4)	0.23917(6)	−0.13423(4)	5.20(1)
I(4)	0.42130(3)	−0.01398(5)	0.34825(3)	4.18(1)
I(5)	0.45616(4)	−0.30293(6)	0.31367(3)	5.13(1)
I(6)	0.38663(4)	0.27460(6)	0.37422(4)	5.58(1)
O(11)	0.2667(4)	0.5444(5)	0.0050(3)	5.0(1)
O(21)	0.7819(3)	0.5015(5)	0.5081(3)	4.7(1)
N(14)	0.1816(4)	0.2860(6)	0.0078(4)	4.3(2)
N(24)	0.6599(4)	0.3002(6)	0.5250(4)	4.7(2)
C(12)	0.1742(6)	0.5145(8)	−0.0610(6)	5.3(2)
C(13)	0.1609(5)	0.3619(8)	−0.0836(5)	4.7(2)
C(15)	0.2766(6)	0.3216(9)	0.0804(5)	5.3(2)
C(16)	0.2852(6)	0.4748(9)	0.0921(5)	5.4(2)
C(22)	0.7131(6)	0.4395(8)	0.4256(5)	4.9(2)
C(23)	0.6308(5)	0.3977(8)	0.4440(5)	4.9(2)
C(25)	0.7381(6)	0.3594(9)	0.6088(5)	5.3(2)
C(26)	0.8163(6)	0.4053(8)	0.5849(5)	4.9(2)
H(1)	0.174(5)	0.211(8)	0.008(5)	4.00
H(2)	0.668(5)	0.223(8)	0.520(5)	4.00

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as follows: (4/3) $[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\ \beta(1,3) + bc(\cos\alpha)\ \beta(2,3)]$.

plied to the data (transmission factors in the range 0.45–1.36). The structure was solved by Patterson and difference Fourier syntheses and refined in full-matrix least squares, the function minimized being $\Sigma w(|F_0| - |F_c|)^2$. Anisotropic displacement parameters were refined for all the nonhydrogen atoms. The hydrogen atoms attached to the nitrogen atoms were refined with fixed isotropic displacement parameters, while all the remaining hydrogens were introduced in the structure model at calculated positions (C–H 0.95 Å) and were unrefined.

Scattering factors were taken from Cromer and Waber [9]. Anomalous dispersion effects were included in F_c; the values for $\delta f'$ and $\delta f''$ were those of Cromer [10]. All calculations were performed on a 80486/33 computer using Personal SDP software [11]. Atomic coordinates, displacement parameters, bond lengths, and angles for **6** have been deposited at the Cambridge Crystallographic Data Centre.

^{13}C NMR Spectra. The spectra were recorded on CH_2Cl_2 solutions at a temperature of 20°C by a Varian FT-NMR spectrometer VXR 300 operating at a 75.4 MHz frequency. DMSO-d_6 ($\delta = 39.70$) was employed as the external reference. Using a 2.5×10^{-2} M donor concentration, diiodine was added stepwise to reach up to a 1:1 donor/I_2 ratio.

Spectrophotometric Measurements and Data Treatments. UV-visible measurements were carried out in CH_2Cl_2 solutions using a Varian model Cary 5 Uv-Vis-Nir spectrophotometer equipped with a temperature controller accessory. The spectra of a number of different solutions were recorded in the 230–550 nm range at 20°C soon after their preparation. Spectra recorded at higher temperatures show modifications in the shape of the bands during the time necessary to thermostat the solutions; therefore, we did not think it convenient to determine the equilibrium constants at variable temperatures, but only at 20°C, since no appreciable changes are verified at this temperature. The criteria used for the choice of reagent concentrations and data treatment have been extensively discussed in Ref. [12].

RESULTS

Solid Compounds

The stoichiometries of the solid diiodine derivatives obtained by reacting **1**·(**2**) and molecular diiodine for 1:1, 1:2, and 1:3 molar ratios in benzene, chloroform, and dichloromethane are reported in Table 2.

In chloroform, the neutral adducts **1**·I_2 (**4**) and **2**·I_2 (**5**) are obtained for the three molar ratios. The same adduct is separated from the 1:1 and 1:2 molar ratios of dichloromethane solutions; whereas, for the 1:3 molar ratio, **1** gives the pentaiodide **8** and **2** the triiodide **7**. The reaction of two substrates differs also in benzene since **1** gives always **4**, while **2** gives **7**. It is interesting to point out that neither **1**$H^+I_3^-$ (**6**) nor **2**$H^+I_5^-$ has been obtained by this method. Morpholinium triiodide, **6**, has been prepared from morpholinium iodide (**1**H^+I^-) and diiodine.

Crystal Structures of **6** *and* **7**. Crystals of **6** derive from the packing of morpholinium cations and triiodide anions, with normal van der Waals interactions between cations and anions (Figure 1).

The asymmetric unit contains two independent cations and two anions, almost related by pseudo B centering symmetry. Such an arrangement should therefore correspond to a primitive lattice defined by the vectors $a' = 1/2(a + c)$, $b' = b$ and $c' = 1/2(a - c)$, where the content of the unit cell is half of that considered here ($Z = 4$ instead of 8), but this is not the case, since the independent cations and anions are not exactly correlated by translations of $1/2a$ and $1/2c$ (Table 3).

The two independent cations are alternately stacked along the [010] direction to form infinite chains of morpholinium ions bound together by hydrogen bonding (see Table 4). The angle between the

TABLE 4 Selected Interatomic Distances (Å) and Angles (deg.) for **6**

I(1)-I(2)	2.969(1)	I(4)-I(5)	2.935(1)
I(1)-I(3)	2.894(1)	I(4)-I(6)	2.899(1)
I(2)-I(1)-I(3)	179.05(2)	I(5)-I(4)-I(6)	177.45(2)
O(11)-C(12)	1.430(8)	O(21)-C(22)	1.424(7)
O(11)-C(16)	1.424(8)	O(21)-C(26)	1.427(7)
N(14)-C(13)	1.503(8)	N(24)-C(23)	1.480(9)
N(14)-C(15)	1.501(9)	N(24)-C(25)	1.489(9)
N(14)-H(1)	0.74(7)	N(24)-H(2)	0.77(7)
C(12)-C(13)	1.508(10)	C(22)-C(23)	1.505(10)
C(15)-C(16)	1.489(10)	C(25)-C(26)	1.503(10)
C(12)-O(11)-C(16)	109.3(5)	C(22)-O(21)-C(26)	111.2(5)
C(13)-N(14)-C(15)	110.7(6)	C(23)-N(24)-C(25)	110.5(5)
O(11)-C(12)-C(13)	111.5(6)	O(21)-C(22)-C(23)	110.3(5)
N(14)-C(13)-C(12)	107.7(5)	N(24)-C(23)-C(22)	109.8(6)
N(14)-C(15)-C(16)	109.4(6)	N(24)-C(25)-C(26)	112.0(5)
O(11)-C(16)-C(15)	112.4(5)	O(21)-C(26)-C(25)	109.0(6)
O(11). . .N(24)′	2.849(7)	O(21). . .N(14)′	2.838(6)
O(11). . .H(2)′	2.13(8)	O(21). . .H(1)′	2.18(8)
O(11). . .H(2)′-N(24)′	157(9)	O(21). . .H(1)′-N(14)′	148(9)

Primed atoms are related to the unprimed ones by the symmetry operation $1 - x$, $1/2 + y$, $1/2 - z$.

TABLE 5 Main FT-IR[a] and FT-Raman[b] bands of solids 4–8 within 200–70 cm^{-1}. IR spectra are recorded as polyethylene pellets.

Compound	*Mode*	*Main Bands below 200 cm*$^{-1}$[a]
4	Raman	157(10), 122(3.7), 75(0.4)
	IR	164*w*, 145*s*, 137*s*, 118*mw*, 95*w*
5	Raman	148(10), 121(2)
	IR	174*s*, 161*s*, 152*s*, 114*m*, 90*w*
6	Raman	115(10), 99(2.6)
	IR	161*ms*, 145*s*, 136*ms*, 126*ms*, 116*s*, 95*ms*
7	Raman	150(0.9), 118(10)
	IR	118*s*, 110*s*
8	Raman	164(10), 135(2.5), 105(1.6)
	IR	164*w*, 142*s*, 104*m*, 79*m*

[a] Symbols: *v* = very, *s* = strong, *m* = medium, *w* = weak.

[b] In the FT-Raman spectra, the values in parentheses represent the intensities of the peaks in relation to the strongest, taken equal to 10.

average molecular planes defined by the carbon atoms of the two independent cations belonging to the same chain is about 73°. The essentially linear triiodide ions fit into the interchain channels extending along [010] and show the usual asymmetry found in most cases, which is probably due to packing effects.

Crystals of compound **7** are monoclinic, space group *Cc* (no. 9), with $a = 15.133(3)$, $b = 10.453(1)$, $c = 8.420(1)$ Å, $\beta = 121.57(1)°$, and $Z = 4$. The structure solution clearly shows the location of the triiodide anion with an average I–I distance of 2.92 Å, while the thiomorpholinium ion is heavily affected by disorder. For this reason, the results of the structure determination are not reported here.

FT-Raman and FT-IR Spectra. The main FT-IR and FT-Raman bands of **4–8** below 200 cm^{-1} are reported in Table 5 and are coherent with the formulation of the compounds (see Discussion).

The FT-Raman spectra have also been carried out on 1:1 mixtures of **1** (or **2**) and I_2 in dichloromethane solutions. Under these conditions, only a broad peak at 164 and 167 cm^{-1} for **1** and **2**, respectively, are recognizable.

The IR spectra of free **1** (or **2**) (a) and mixtures of **1** (**2**) and I_2 in 1:1 (b) and 1:2 molar ratios (c) have also been recorded in the NH absorption range 3400–3250 cm^{-1} in dichloromethane solution and are reported in Figure 3. The two bands at 3345 and

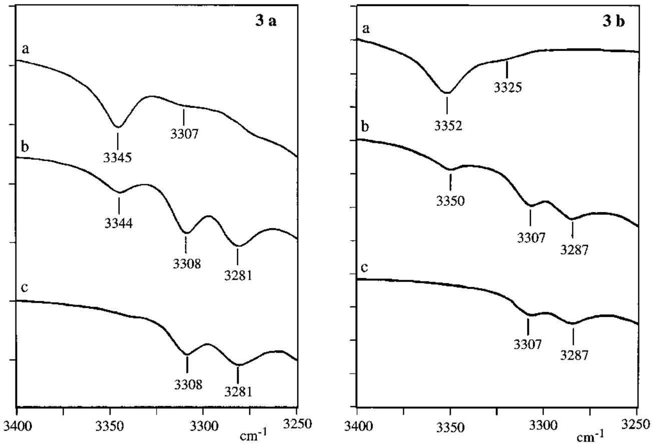


FIGURE 3. IR ν(N–H) absorptions of morpholine (**1**) and thiomorpholine (**2**) solution of CH_2Cl_2 in presence of different amounts of diiodine. **3a**, [**1**] = 5.0×10^{-2} M; [I_2] = 0 (*a*), 2.5×10^{-2} (*b*), and 5.0×10^{-2} (*c*) M. **3b**, [**2**] = 5.0×10^{-2} M; [I_2] = 0 (*a*), 2.5×10^{-2} (*b*), and 5.0×10^{-2} (*c*) M.

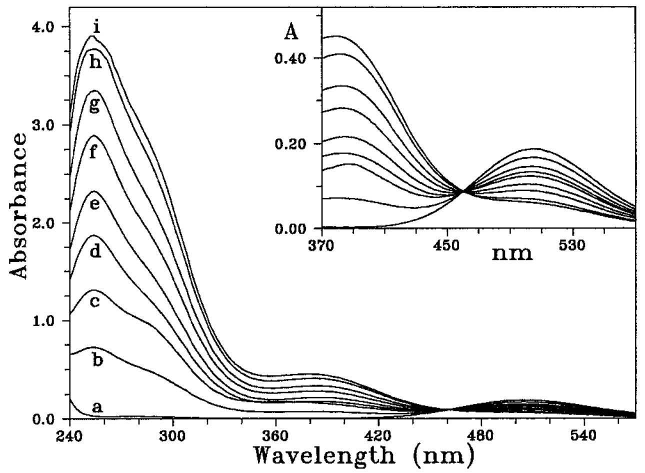


FIGURE 4. UV spectra of thiomorpholine (**2**) and its diiodine mixtures in CH_2Cl_2 solutions at 20°C. [I_2] = 2.02×10^{-4} M; [**2**] = 0, 5.17×10^{-5}, 1.03×10^{-4}, 1.55×10^{-4}, 2.07×10^{-4}, 3.10×10^{-4}, 4.14×10^{-4}, 6.20×10^{-4}, and 8.27×10^{-4} M from *a* to *i*, respectively. The zoomed area shows the isosbestic point falling at 460 nm between the visible band of the free I_2 and its blue-shifted band.

3307 cm^{-1} in **1** and at 3352 and 3325 cm^{-1} in **2** have been assigned to equatorial and axial ν(N–H) conformers, respectively [13]. The addition of I_2 to **1** (or **2**) solutions up to the 1:2 molar ratio causes complete disappearance of the equatorial ν(N–H)s and the appearance of two new absorptions at 3308 and 3281 cm^{-1} in **1** – I_2, and 3307 and 3287 cm^{-1} in **2** – I_2 mixtures, which can be similarly attributed to the equatorial and axial ν(N–H) of the adducts. From the related transmittances of Figure 3, one can see that in **1** or **2**, N–H is prevalently axial, whereas in both adducts it is ca. 50% axial and 50% equatorial.

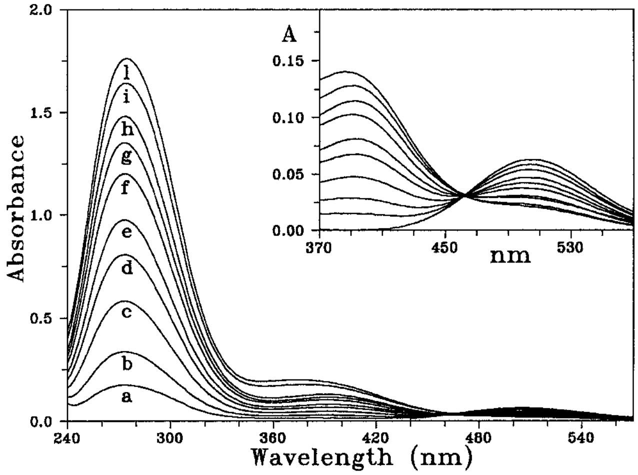


FIGURE 5. UV spectra of *N*-methylmorpholine (**3**) and its diiodine mixtures in CH_2Cl_2 solutions at 20°C. [I_2] = 7.05×10^{-5} M; [**3**] = 1.33×10^{-5}, 3.32×10^{-5}, 6.64×10^{-5}, 9.97×10^{-5}, 1.33×10^{-4}, 1.99×10^{-4}, 2.66×10^{-4}, 3.32×10^{-4}, 5.54×10^{-4}, and 8.30×10^{-4} M from *a* to *l*, respectively. The zoomed area shows the isosbestic point falling at 462 nm between the visible band of the free I_2 and its blue-shifted band.

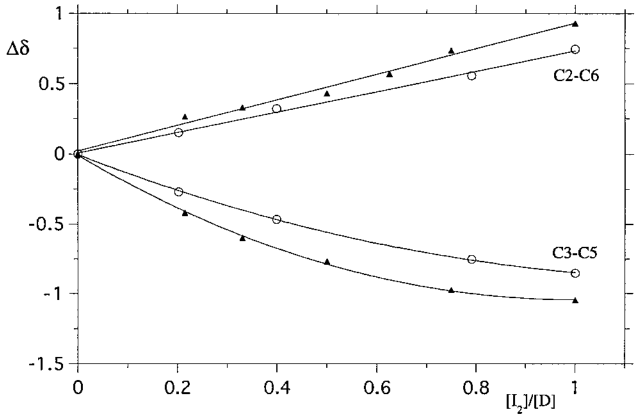


FIGURE 6. The $\Delta\delta$ values (chemical shifts measured on solutions at different diiodine/donor ratios minus chemical shifts of the free donor) of carbons C2-C6 and C3-C5 as a function of the [I_2/D] molar ratio for morpholine (▲) and thiomorpholine (○), respectively. [**1**] = 2.5×10^{-2} M, δ(C2-C6) = 46.39; δ(C3-C5) = 68.01. [**2**] = 2.5×10^{-2}M, δ(C2-C6) = 27.45; δ(C3-C5) = 46.99.

UV-Visible. The equilibrium (1) using **1** as a donor has already been investigated in solution [14]. Besides **2**, we have also studied *N*-methylmorpholine (**3**) to introduce further details in studying the reactivity of these compounds in solution. Addition of diiodine to the solutions of **2** or **3** produces two pronounced peaks in the UV-visible spectra. The visible diiodine band shifts toward shorter wavelengths, and a new band, due to a charge transfer transition,

TABLE 6 Molar extinction coefficients ε at six wavelengths λ used for calculation, association constants *K* at 20 °C, and sums of the squared deviations χ^2 for the reaction between compounds thiomorpholine **2** and *N*-methylmorpholine **3** with I_2 in dichloromethane.[a]

Compound	λ (nm)	ε ($dm^3\ mol^{-1}\ cm^{-1}$)	*K* ($dm^3\ mol^{-1}$)	χ^2	Ref.
1			1,781		[14]
2	245	20,700 (120)			
	255	23,000 (170)			
	270	19,600 (100)			
	290	14,800 (100)	8,500 (250)[c]	0.4	This work
	310	8,500 (70)			
	380	2,370 (30)			
3	250	15,000 (100)			
	270	29,600 (200)			
	290	24,600 (100)			
	310	12,600 (60)	8,400 (150)[c]	0.04	This work
	350	2,300 (35)			
	400	2,580 (35)			
1,4-Dithiane			50		[19]
1,4-Dioxane[b]			~1		[19]
1,4-Thioxane[b]			73		[19]

[a] Standard deviations in parentheses.
[b] *K* values obtained in CCl_4.
[c] Mean value of the *K*s calculated at the six wavelengths.

appears in the ultraviolet region. The existence of an isosbestic point between the visible band of free diiodine and its blue shifted band agrees with the presence of the equilibrium (1) (see Figures 4 and 5 for the mixtures of diiodine with **2** or **3**, respectively. Since these mixtures lack stability in time at temperatures >20°C (see experimental), the thermodynamic parameters were not determined.

The formation constant, *K*, and the molar extinction coefficients obtained at 20°C for **2** and **3** are shown in Table 6 together with the *K* values of other related heterocyclic compounds.

^{13}C NMR Spectra. The ^{13}C NMR spectra of **1** and **2** show two resonances of carbons C2-C6 and C3-C5. At room temperature, the ring interconversion and the nitrogen atom inversion are fast processes, and only the average of these conformations is observed in the NMR timescale [15]. The spectra of several solutions of two reagents, obtained by adding increasing amounts of diiodine to a constant concentration of **1** or **2**, were recorded in dichloromethane solutions. In Figure 6, the diagram of the chemical shift variations $\Delta\delta$ ($\Delta\delta$ = chemical shift measured for solutions at different $[I_2]/[D]$ ratios minus chemical shifts of the free donor) is reported versus $[I_2]/[D]$ up to a 1:1 ratio. The $\Delta\delta$ of the couple C2-C6 increases, whereas that of the couple C3-C5 decreases, as $[I_2]/[D]$ increases.

DISCUSSION

Solid State

Compounds **4** and **5** did not give suitable crystals for X-ray structure determination, and their structures were inferred from analytical data and IR and Raman spectra. For weak or medium-weak adducts ($D\cdots I_2$ bond order lower than ~0.4) [16], only one ν(I–I) Raman band shifted to lower frequencies than the value in the solid I_2 was found [17]. When the interaction is strong, the three-body model, D–I–I (bond orders of both D–I and I–I in the range ~0.4–0.6), must be applied in order to foresee the vibrations, and three Raman and IR active vibrations [the symmetric (ν_1) and antisymmetric (ν_3) stretchings and the (ν_2) bending] are expected [6]. Two Raman bands in the spectra of **4** at 157 (10) and 122 (3.7) cm^{-1} and in that of **5** at 148 (10) and 121 (2) cm^{-1}, with their IR analogs at 164*w* and 118*mw* cm^{-1} for 14 and 152*s* and 114*m* cm^{-1} for **5** (Table 5), attributable to ν_3 and ν_1 of N–I–I group, suggest that both compounds can be considered strong adducts.

As expected, the crystal structure of **6** shows the morpholine ring in the usual chair conformation with the morpholinium units bound by hydrogen bonds to form linear chains. The two independent I_3^- anions present in the unit cell are similar and poorly asymmetric. Accordingly, only one strong FT-Raman band at 115 cm^{-1} is found.

This Raman spectrum is completely different from that recorded for compound **8**, which had been previously characterized both by X-ray and FT-Raman spectroscopy [7]. The authors describe the I_5^- anion as a weak adduct between I_2 and an asymmetric I_3^-. Accordingly, Raman bands at 135 (2.5) and 105 (1.6) cm^{-1} (142*s* and 104*m* cm^{-1} in the infrared spectrum) have been attributed to the asymmetric I_3^-, while that at 164 (10) cm^{-1} (164*w* cm^{-1} in the infrared spectrum) to the ν(I–I) of the perturbed diiodine molecule.

As for **6**, compound **7** shows a strong FT-Raman band at 118 cm^{-1}, which is indicative of a triiodide. This is also confirmed by the X-ray crystal structure determination.

Solution

Although in dichloromethane solutions (see Table 2) **2** gives neutral **5** and ionic **7** compounds, the isosbestic point for the mixtures of **2** and I_2 (Figure 4) shows that the 1:1 adduct is the species predominant in the range of investigated concentrations. The same is verified for mixtures of **3** and I_2 (see Figure 5), and, in both cases, the 1:1 model fits the experimental absorbances very well. On the basis of the *K* values reported in Table 6, a coordination through the nitrogen must be hypothesized for both. In fact, adducts of I_2 with heterocyclic compounds such as 1,4-dithiane [19], 1,4-dioxane [19], and 1,4-thioxane [19] have *K* values very different from those of **1–3**. Further evidence for the *N*-coordination arises from the changes in the ν(N–H) vibrations of the infrared spectra of **1** and **2** in the presence of diiodine (see Results and Figure 3) and from ^{13}C NMR experiments. The adduct formation deshields C2 and C6 and shields C3 and C5 (see Figure 6). The values of $\Delta\delta$ for $\mathbf{1}\cdot I_2$ (0.93 and -1.05 ppm) and $\mathbf{2}\cdot I_2$ (0.75 and -0.85 ppm) show the same trend as in the adduct [16] between **1** and BH_3 ($\Delta\delta = 6.74$ and -0.95 ppm for C2-C6 and C3-C5, respectively) and indicates an interaction of **1** and **2** with I_2 weaker than that with BH_3. Raman frequencies at 164 and 167 cm^{-1} found for $\mathbf{1}\cdot I_2$ and $\mathbf{2}\cdot I_2$, respectively, in CH_2Cl_2 solution are higher than in the solid state; the little shifts with respect to free diiodine (209 cm^{-1} in CH_2Cl_2 solution) confirm the nature of weak adducts between these substrates and diiodine in solution.

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