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Molecular Complexes of Quinolines with Iodine

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1 : 1 Charge-transfer molecular complexes of some quinolines with iodine as a σ-electron acceptor were synthesized and charcterized. The spectral characteristics and stability of the formed charge-transfer comlexes were determined and are discussed in terms of the basicity and molecular structure of the donor as well as the solvent polarity. It is deduced that such factors as the n-donor strength, steric effect, and solvent polarity play operative roles in determining the stability of these CT complexes. The formed complexes are ascertained to be of a strong n–σ kind.

Azaaromatic compounds are generally a particularly intersting class of donor molecules, because they can function as n- and Π-donors. Accordingly, charge-transfer (CT) molecular comlexes of quinoline compounds, as an example of azines, have been subjected to many studies involving Π-electron acceptors.[1—7] However, little attention has been paid to CT complexes of quinolines with σ-electron acceptors,[8—12] where the literature is still scarce of detailed studies concerning their CT complexes with the σ-electron acceptor iodine. Therefore, the present investigation was devoted to carrying out a systematic study of the CT molecular complexes of some quinoline derivatives (quinoline, 6-methyl-, 6-methoxy-, 2, 6-dimethyl-, and 3-bromoquinoline) with iodine. The spectral characteristics, thermodynamic parameters of complex formation and stability of the formed complexes were examined and are discussed in terms of the donor molecular structure as well as the nature of the organic solvent used. Further, the study involved a synthesis and characterization of these molecular complexes.

Experimental

Material and Solutions. The quinoline derivatives employed were Aldrich reagents with high purity and were used without further purification. Iodine (Analar grade BDH) was resublimed before use. Chloroform, dichloromethane, and dichloroethane(spectroscopy grade solvents) were distilled before use by standard methods[13] and stored over molecular sieves (4 Å) and calcium chloride.

Stock solutions of the donors and iodine were freshly prepared by dissolving accurately weighted amounts in the deoxygenated solvent prior to use. The stock of iodine solution was stored in the dark. Solutions for spectrophotometric measurements were prepared by accurate dilution of the stock solutions. The exact concentration of the iodine solution was checked spectrophotometrically.

Physical Measurements. The electronic spectra of the examined CT complex solutions were recorded on a Bausch & Lomb spectrophotometer using matched silica cells of 1.0 cm path length. Temperature control was achieved by using a JULABO FP 40 ultratemperature thermostated cell holder with an accuracy of ±0.05 °C. The infrared spectra of the isolated solid CT molecular complexes were taken on a Shimadzu 470 IR-spectrophotometer. Computations were performed on an Apple IIe microcomputer with the aid of two programs based on unweighted linear least-squares fits. The ionization potential values of the subjected quinolines were determined by applying a photoelectron spectroscopy technique at the laboratory of professor G. Pfister-Guillouzo, University of Pau, Pau, France.

Synthesis of the Solid Charge-Transfer Complexes. Equimolar saturated solutions of each donor and iodine in dichloromethane were mixed. The mixtures were kept for 24 h where the CT complexes were precipitated and the solvent was removed by filtration. The separated solid complexes were washed, collected, and dried. Elemental analyses data (C, H, N) of the isolated complexes along with some of their physical properties (color, melting points) are listed in Table 1.

Results and Discussion

The electronic absorption spectra of dichloromethane solutions of iodine and each of the quinolines under investigation were recorded in the wavelength range 350—650 nm (Fig. 1). Generally, such spectra do not exhibit any noticeable variations in intensity with time. Herein, it is worthwhile to report that the subjected

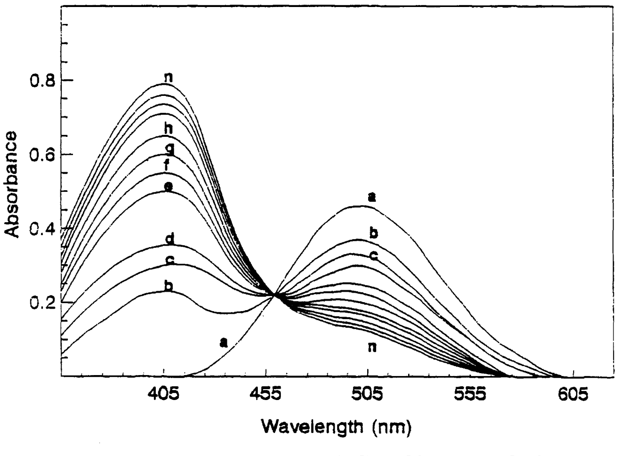

Fig. 1. Electronic spectra of CH_2Cl_2 6-methylquinoline–iodine complex solutions at 25 °C. [iodine]= 4.79×10^{-4} mol dm^{-3}; curve a. [donor]=2.015, 3.02, 4.03, 6.04, 8.06, 10.0, 12.0, 14.0, 16.0, 18.0 and 20.0×10^{-3} mol dm^{-3}; curves b, c, d, e, f, g, h, k, l, m, and n.

Table 1. Elemental Analyses Data and Some Physical Properties of the Synthesized CT Complexes of Quinoline Derivatives with Iodine

Complex	Mp °C	Color	% Calcd (Found) C	H	N
Quinoline–I_2	66	Green	28.20 (28.53)	1.80 (1.72)	3.65 (3.54)
6-Methylquinoline–I_2	75	Brown	30.20 (30.45)	2.26 (2.01)	3.50 (3.60)
6-Methoxyquinoline–I_2	117	Deep green	29.05 (29.32)	2.18 (2.29)	3.39 (3.32)
2,6-Dimethylquinoline–I_2	105	Deep brown	32.11 (32.30)	2.67 (2.52)	3.40 (3.10)
3-Bromoquinoline–I_2	68	Pink	23.38 (23.58)	1.30 (1.29)	3.03 (2.95)

quinolines have no absorptions within this wavelength range. It is evident that the broad band located at 500 nm, which is due to the $4\Pi_g \rightarrow 10\sigma_u^*$ electronic transition in free iodine,[14] exhibits a hypsochromic shift due to complexation with the added quinoline compound. Meanwhile, the intensity of the blue-shifted iodine band increases, whereas that of the free iodine band decreases as the concentration of the quinoline donor is increased. The observed blue shift in the free iodine band upon complexation could be attributed to a perturbation of the iodine molecular orbital (σ_u^*) by a repulsive interaction between the iodine molecule and its partner donor molecule in the complex.[14,15] Accordingly, a more repulsion (energy) interaction would result in a large blue shift of the iodine band. It is therefore reasonable to consider the extent of the blue shift in the iodine band as being a measure of the magnitude of the interaction between the donor and the iodine molecule. An examination of Table 2 reveals that the observed blue shift in the iodine band increases by changing the nature of the donor according to the following sequence: 6-methylquinoline>6-methoxyquinoline>quinoline>2,6-dimethylquinoline>3-bromoquinoline. For each donor, a clear isosbestic point appears (Fig. 1), indicating the formation of one species of CT complex which is in equilibrium with the uncomplexed iodine and quinoline donor ($D+I_2 \rightleftarrows DI_2$).

Equilibrium Constant Values. The equilibrium constant (K_{CT}) and molar extinction coefficient (δ_{CT}) values at 25 °C in dichloromethane for the formed CT complexes were computed from the observed increase in the absorbance of the blue-shifted iodine band by increasing the donor concentration at a constant initial iodine concentration. The absorbance was measured against iodine of the same initial concentration as the reference. Bensi–Hildebrand[16] and Scott[17] equations were adopted for such calculations. The equilibrium constant values obtained from the two methods are in good agreement and the average values are cited in Table 2. A careful examination of the table reveals that the equilibrium constant value decreases, in terms of the nature of the electron donor, according to the following sequence: 6-methylquinoline>6-methoxyquinoline>quinoline>2,6-dimethylquinoline>3-bromoquinoline. With the exception of the donor 2,6-dimethylquinoline, one can generally deduce that the stability of the formed CT complex increases as the basic strength of the donor (expressed in pK_a values[18]) is increased. Further, the above-described large blue shift in the iodine band (as a measure of the amount of CT-interaction, i.e., complex formation) increases as the basicity of the quinoline donor is increased. This behavior suggests that quinolines mainly behave as n-donors, where one should expect a high stability of the CT complex as the basicity of quinoline compound is increased. Good convincing evidence for this conclusion can be attained from the observation that the stability of the formed CT complexes increases as the experimentally determined n-ionization potential of the quinoline donor is lowered (cf. Table 2). Accordingly, one can deduce that the CT complexes formed from the interaction of quinolines with iodine are of the n–σ kind. With respect to the observed unexpected behavior of the donor 2,6-dimethylquinoline, though this donor is characterized by high basicity and a low n-ionization potential (i.e., high electron n-donor ability), its formed CT complex with iodine is characterized by low stability compared to the other examined quinolines, which are characterized by relatively low basicity and high n-ionization potentials. This behavior can likely be explained based on the principle of the steric effect of the bulky methyl group substituted at position 2. This reflects, itself, in an effective shielding of the nitrogen atom, thereby reducing the approachability of the iodine molecule i.e., weak intermolecular CT interactions. The above-deduced n–σ nature for the I_2–quinolines CT complexes could be further substantiated by the observation that the obtained K_{CT} values for these CT complexes are higher than those reported for the corresponding ones with the Π-electron acceptors.[1] On the other hand, these values are much more in line with those for other n–σ complexes.[11,12]

The thermodynamic parameters (ΔH, ΔG, and ΔS) associated with the CT complex formation of 2,6-di-

Table 2. Spectral Characteristics and Computed Equilibrium Constants (K_{CT}) and Molar Extinction Coefficients (δ_{CT}) of Iodine–Quinolines CT Complexes in CH_2Cl_2 at 25 °C along with the pK_a and n-Ionization Potential (IPn) Values of Quinolines

Compound	Blue-shifted band of iodine	K_{CT}[a)]	δ_{CT}[a)]	pK_a	IPn
	(λ_{nm})	$mol^{-1}\,dm^3$	$mol^{-1}\,cm^{-1}\,dm^3$		eV
Quinoline	384	93.66	899.50	4.88	9.46
6-Methylquinoline	380	192.48	1002.96	5.17	9.23
6-Methoxyquinoline	382	184.50	670.05	5.03	9.24
2,6-Dimethylquinoline	392	66.39	1865.20	6.00	9.09
3-Bromoquinoline	404	25.14	2168.62	2.69	9.65

a) Standard deviation of $K_{CT}=\pm1.18\%$ and of $\delta_{CT}=\pm2.0\%$.

Table 3. Thermodynamic Parameters of Iodine–2,6-Dimethylquinoline CT Complex in $CHCl_3$

Temperature	K_{CT}[a)]	δ_{CT}[a)]	$-\Delta H$	$-\Delta S$	$-\Delta G$	b^2/a^2
°C	$mol^{-1}\,dm^3$	$mol^{-1}\,cm^{-1}\,dm^3$	$K\,cal\,mol^{-1}$	$cal\,mol^{-1}$	$K\,cal\,mol^{-1}$	
10	92.43	2076.59				
15	84.67	1970.36				
20	71.76	1947.45				
25	55.19	1975.34				
			5.72	11.13	2.39	0.079

a) Standard deviation of $K_{CT}=\pm1.2\%$ and of $\delta_{CT}=\pm2.0\%$.

Table 4. Spectral Charcteristics and the Computed K_{CT} and δ_{CT} Values of the CT Complex: Iodine-6-Methylquinoline in Different Solvents at 25 °C

Solvent	D[a)]	Blue-shifted band of iodine	K_{CT}[b)]	δ_{CT}[b)]
		(λ_{nm})	$mol^{-1}\,dm^3$	$mol^{-1}\,cm^{-1}\,dm^3$
$CHCl_3$	4.08	387.0	70.26	1250.28
CH_2Cl_2	9.08	380.0	192.48	1002.96
$C_2H_4Cl_4$	10.65	378.5	212.89	901.35

a) D=The dielectric constant of the solvent; b) Standard deviation of $K_{CT}=\pm1.6\%$ and of $\delta_{CT}=\pm2.1\%$.

methylquinoline with iodine were evaluated (Table 3). For this purpose, the K_{CT} values of this complex at 10, 15, 20, and 25 °C were determined in chloroform using the same procedure as discussed above. The obtained results (Table 3) reveal that the formed complex is better stabilized as the temperature is lowered. This indicates the exothermic nature of the CT complex formation process of the system under investigation. The enthalpy (ΔH) was determined from the computed K_{CT} values at different temperatures making use of the van't Hoff plots of $\log K_{CT}$ vs. $1/T$. The Gibbs free energy (ΔG) was calculated from the following equation: $\Delta G=-RT\ln K_{CT}$. The entropy change (ΔS) was also determined. The obtained values for ΔH, ΔS, and ΔG are of the same magnitude as those reported for strong n–σ complexes.[11,12,19] This could be supported by the determined b^2/a^2 ratio using the relation $b^2/a^2=-\Delta H/h\bar{\nu}$, where a and b are the coefficients of the dative and no-bond functions of the ground-state wave function of the CT complex. $\bar{\nu}$ is the wavenumber (cm^{-1}) of the blue-shifted band of iodine. The obtained ratio is compared to those of many strong CT complexes.[20—22]

Solvent Effect. In order to investigate the effect of solvents on the CT interaction between quinolines and iodine, the electronic absorption spectra of the 6-methylquinoline–iodine complex were investigated in different solvents having various polarities viz. $CHCl_3$ ($D=4.08$), CH_2Cl_2 ($D=9.08$), and $C_2H_4Cl_2$ ($D=10.65$) at 25 °C. The computed K_{CT} and δ_{CT} values with the λ_{max} of the blue-shifted iodine band are listed in Table 4. The results indicate that the stability of the formed CT complex increases as the dielectric constant of the solvent is increased ($CHCl_3 \rightarrow CH_2Cl_2 \rightarrow C_2H_4Cl_2$). This behavior could be substantiated by the observed large blue shift in the iodine band along the same sequence. This can be interpreted based on the principle of high stabilization of the ground state of the complex upon increasing the solvent polarity. This is due to the increased interaction between the dipole of the complex and that of the solvent, which is in accordance with the strong nature of the investigated CT complexes (i.e., n–σ kind). In this respect, it is worth mentioning that none of the solvents used possessed a basic character sufficient for competition with the studied quinoline bases. Furthermore, specific interactions of the employed solvents with the investigated complexes or the donors were of the minor importance.[12)]

Characterization of the Isolated Solid Com-

plexes. Elemental analyses data (C, H, and N contents) of the prepared solid CT complexes along with some of their physical properties are cited in Table 1. The data clearly indicate the formation of 1 : 1 CT complexes. A careful examination of the infrared spectra of the synthesized complexes as well as those of free donors reveal that the $\nu_{\mathrm{C=C}}$ bands belonging to the donor molecules (1420—1500 cm^{-1}) were slightly shifted to lower frequencies, or more or less unchanged upon CT complex formation. Moreover, a distinct $\nu_{\mathrm{C=N}}$ stretching of the donors (1570—1620 cm^{-1}) exhibited a marked shift to lower frequencies (1530—1600 cm^{-1}) upon complexation. Further, the intensity as well as the shape of the $\nu_{\mathrm{C=N}}$ band were also markedly changed. This behavior suggests that the participation of the C=N group in the charge migration to the electron acceptor iodine is more pronounced. Otherwise, the participation of C=C bonds in this interaction seems to be less important. This provides an additional evidence for the *n*–σ nature of the CT complexes under investigation.

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