Russian Journal of General Chemistry, Vol. 75, No. 3, 2005, pp. 402–408. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 3, 2005, pp. 438–444.

Molecular Complexes of Iodine with Aromatic Compounds

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Received July 11, 2003

Abstract—The correlation between the spectral characteristics of molecular complexes of iodine with various benzene derivatives and the ionization potentials of the donor molecules is discussed. The isomerism of these complexes, determined by the structure of the electronic level with which the orbital of the acceptor interacts and by the steric structure of the donor molecules, is revealed.

The energies ($h\nu$) of charge-transfer transitions in molecular complexes linearly correlate with the ionization potentials (IP) of the donor components [1]:

$$h\nu = a\mathrm{IP} + b. \tag{1}$$

This function describes the correlation between a property of a complex system ($h\nu$) and a property of its component (IP). Therefore, analysis of this equation as applied to a wide set of complexes of the same acceptor will reveal other factors affecting $h\nu$ of the complexes. One of such factors may be the structure of the complex.

Initially [2] examination of this dependence for molecular complexes of iodine revealed no effect of the molecular structure of the organic donors and of the type of interaction between the components (according to Mulliken's classification) on the parameters of (1). In the subsequent papers [2, 3], it was realized that the molecular structure of the donors should be taken into account. It is also important that the type of the ionization potential in this equation remains unclear. Previous analysis of Eq. (1) as applied to a wide set of complexes of *sym*-trinitrobenzene [4] led to the following conclusions. First, the correlation should contain the adiabatic ionization potential. Second, the wide set of complexes of aromatic donors with *sym*-trinitrobenzene cannot be described by a single linear equation (1).

The goals of this work were to analyze the linear correlation (1) as applied to molecular complexes of iodine with aromatic donors (π–σ complexes, according to Mulliken's classification [1]) and to study how the structure of the components and the type of the ionization potential affect the coefficients a and b in this equation.

The positions of the maxima of the charge-transfer bands in the spectra of molecular complexes of iodine (results of this work and published data) and the ionization potentials of the donor molecules are given in Table 1. According to numerous published data, the composition of these complexes is 1 : 1. In this paper, the correlation and regression analyses of (1) are performed both for the whole set of the complexes and for their particular groups (Table 1), using both adiabatic ($\mathrm{IP_a}$) and vertical ($\mathrm{IP_v}$) ionization potentials of the donor molecules (Table 2). The first and second charge-transfer bands are analyzed in relation to the first and second ionization potentials of the donor components of the complexes. The published correlations $\lambda_1 \sim f(\mathrm{IP}_1)$ and $\lambda_2 \sim f(\mathrm{IP}_2)$ are not always valid. The correlations for particular groups of complexes have better quality with the adiabatic ionization potentials than with the vertical potentials. This fact suggests changes in the structures of the donor molecules in the complexes, compared to the structures of the donor molecules taken separately. The changes are possible in the bond lengths, bond angles, and torsion angles for those donors for which $\mathrm{IP_a} \neq \mathrm{IP_v}$. Only in this case the vibrational state of the molecules changes and their structure becomes distorted. The parameters of (1) for the whole set of the complexes are unsatisfactory irrespective of the type of the ionization potential. Several groups of complexes are distinguished: benzene $\pi(b_1)$–σ complexes, benzene $\pi(a_2)$–σ complexes, sterically hindered benzene $\pi(b_1)$–σ complexes, and diphenyl $\pi(b_1)$–σ complexes. The names of these groups include the name of the aromatic system common for all the donors of this group and the types of the interacting orbitals of the donor and acceptor. For the orbitals of the donor, the symmetry is also indicated. Some of these groups of complexes are analogs of the groups of complexes with other acceptors, studied previously [4, 25].

The first group of benzene complexes, $\pi(b_1)$–σ, is the largest (Table 1). It includes complexes of iodine

Table 1. Positions of maxima of the charge-transfer bands in the spectra of molecular complexes of iodine and ionization potentials of the aromatic donors

Donor	Charge-transfer band maximum, nm	Ionization potential^a of donor [5–8], eV	
		IP_a	IP_v
Benzene $\pi((b_1)–\sigma$ group			
Benzene	260^b [9]	9.241	9.241
Toluene	301^c	8.82	8.85
	302 [10]		
	304 [11]		
o-Xylene	316 [10]	8.56	8.57
	317 [11]		
m-Xylene	318 [10, 11]	8.56	8.55
1,3,5-Trimethylbenzene	332 [10, 12]	8.40	8.42
	334 [11]		
Hexamethylbenzene	371 [12]	7.85	7.85
	375 [10, 13, 14]		
	376 [11]		
Ethylbenzene	304 [11]	8.76	8.77
1,2-Diphenylethane	304 [10]	(8.76)	–
n-Propylbenzene	305 [11]	8.71	–
Isopropylbenzene	301^c	8.69	8.71
	304 [11]		
n-Butylbenzene	305 [11]	8.69	–
tert-Butylbenzene	305 [11]	8.725	–
Styrene	330 [10]	8.42	8.48
	333 [11]		
(*E*)-1-Phenyl-1-propene	349 [11]	8.20	8.37
Anisole	345 [15, 16]	8.22	8.42
	347 [11]		
1,4-Dimethoxybenzene	403 [11]	7.505	7.90
	404 [15]		
Dibenzo-*p*-dioxin	399.5 [17]	7.598	7.78
Phenol	321^c	8.50	8.67
Fluorobenzene	282 [18]	9.11	9.11
	288 [19]		
1,3-Difluorobenzene	280^b [19]	9.32	9.5
1,4-Difluorobenzene	278 [18]	9.159	9.40
1,2,4-Trifluorobenzene	278 [19]	9.304	9.50
Chlorobenzene	282 [18]	9.10	9.09
	283 [11]		
2-Chlorotoluene	298 [11]	8.83	8.97
3-Chlorotoluene	298 [11]	8.83	8.80
Bromobenzene	286 [18]	9.03	9.05
	288 [11]		
	290 [10]		
3-Bromotoluene	298 [11]	8.77	8.77

Donor	Charge-transfer band maximum, nm	Ionization potential^a of donor [5–8], eV	
		IP_a	IP_v
Benzene $\pi(a_2)–\sigma$ group			
Benzene	291 [16, 20]	9.241	9.241
	292 [10, 11, 18]		
	295 [9, 12]		
	296 [19]		
	297^d [21]		
Anisole	295 [15]	(9.21)	9.21
	296 [16]		
1,4-Dimethoxybenzene	295 [15]	(9.21)	9.30 [22]
Phenol	289^c	9.28	9.28
Diphenyl	302 [15]	9.08	9.22
p-Xylene	302^c	9.05 [23]	9.05 [23]
	304 [10, 11]		
1,2,4-Trimethylbenzene	318^c	(8.80)	8.95
1,2,3,4-Tetramethylbenzene	333 [11]	(8.57)	8.57
1,2,3,5-Tetramethylbenzene	339 [12]	(8.48)	–
1,2,4,5-Tetramethylbenzene	332 [10, 11]	(8.59)	8.68
	333^c	(8.57)	
Pentamethylbenzene	355 [12]	(8.27)	–
	357 [10]	(8.24)	
p-Cymene	305 [11]	(9.02)	–
Hexachlorobenzene	308^c	8.98	9.19
1,3,5-Trifluorobenzene	274 [19]	9.64	9.8
	302^b [18]		
4-Chlorotoluene	291 [11]	(9.28)	9.28
4-Bromotoluene	295 [11]	(9.21)	–
Group of sterically hindered benzene $\pi((b_1)–\sigma$ complexes			
Tetralin	317^c	8.40 [22]	8.40 [22]
1,3,5-Triethylbenzene	335 [24]	–	8.32
1,3,5-Tri-*tert*-butylbenzene	338 [24]	–	8.19
Hexaethylbenzene	375 [12, 24]	–	7.71
	378 [10]		
	379 [11]		
2,6-Di-*tert*-butyl-4-methylphenol	382^c	–	7.80
Group of sterically hindered benzene $\pi(a_2)–\sigma$ complexes			
2,6-Di-*tert*-butyl-4-methylphenol	322^c	–	8.50

Table 1. (Contd.)

Donor	Charge-transfer band maximum, nm	Ionization potential[a] of donor [5–8], eV		Donor	Charge-transfer band maximum, nm	Ionization potential[a] of donor [5–8], eV	
		IP_a	IP_v			IP_a	IP_v
1,2-Dibromobenzene	286 [18]	(9.07)	8.99	*Diphenyl $\pi((b_1)$–σ group*			
1,3,5-Tribromobenzene	276 [18]	9.21	9.21	Diphenyl	340 [21]	7.95	8.32
β-Bromostyrene	310 [11]	(8.67)	–				
1,2-Diiodobenzene	288 [18]	(9.03)	–				

[a] The ionization potentials of the donors are taken from [5–8], unless otherwise indicated. The adiabatic values calculated in this work by the correlation equations are given in parentheses. [b] Not used in correlation analysis; for explanations, see text. [c] Obtained in this work. [d] Excluded because of the large deviation from the calculated value [Eq. (1)].

Table 2. Correlation analysis of Eq. (1) for iodine complexes

Correlation parameter	IP type	Data of [13]	Whole set of complexes	Benzene group		Group of sterically hindered benzene $\pi(b_1)$–σ complexes
				$\pi(b_1)$–σ	$\pi(a_2)$–σ	
Coefficiebt *a*	IP_a	0.67	0.7473	0.8403	0.7561	–
	IP_v	–	0.7029	0.8866	0.7613	0.8261
S_a^2	IP_a	–	0.0005288	0.0001926	0.001679	–
	IP_v	–	0.0005347	0.001076	0.001930	0.005855
Coefficient *b*	IP_a	–1.9	–2.517	–3.285	–2.757	–
	IP_v	–	–2.212	–3.739	–2.837	–3.101
S_b^2	IP_a	–	0.03969	0.01409	0.1423	–
	IP_v	–	0.03978	0.07998	0.1612	0.3700
Correlation coefficient *r*	IP_a	–	0.9736	0.9946	0.9801	–
	IP_v	–	0.9617	0.9737	0.9638	0.9752
Variance S^2	IP_a	–	0.006663	0.001742	0.0005788	–
	IP_v	–	0.01473	0.009449	0.003146	0.003804
Sample size *n*	IP_a	–	60	42	16	–
	IP_v	–	77	42	25	8

with benzene, some of its alkyl derivatives, styrene and its derivatives, and a series of oxygen and halogen derivative of benzene. In the electronic spectra, complexes of this group give the first (long-wave) bands. The σ orbital of the acceptor in complexes of this group interacts with the $\pi(b_1)$ orbital of the donor molecule, as the ionization potentials of the donors used in the correlation analysis [Eq. (1)] correspond just to orbitals of this type and symmetry. This orbital is the highest occupied molecular orbital (HOMO) of the donors. It has nodes between the C^2 and C^3, and between the C^5 and C^6 atoms of the aromatic ring and a node between the atom of the substituent at C^1 and the C^1 atom of the aromatic ring.

The structure of the benzene–iodine complexes was studied and discussed in numerous papers [26]. The acceptor coordinates with the π system of the donor molecule. The aniline complex does not belong to this group of complexes. In this complex, the iodine σ orbital interacts not only with the π system of the aromatic ring, but also with the lone electron pair of nitrogen [27]. However, complexes of alkoxy and hydroxy derivatives of benzene, according to our analysis, do belong to the benzene $\pi(b_1)$–σ group, which suggests that the iodine orbital does not interact with a lone electron pair of the oxygen atom, because of the weaker donor power of oxygen compared to nitrogen; the interaction with the π system of the aromatic ring is preserved. This group also includes the complex of iodine with dibenzo-*p*-dioxin, although previously [17] it was suggested that the iodine molecule coordinates with the oxygen atoms (n–σ complex according to Mulliken classification). The first ionization potential of dibenzo-*p*-dioxin corresponds to the ionization from the $\pi(b_1)$ orbital [5], and the charge-transfer band in the spectrum of its complex well fits linear equation (1) obtained for the benzene $\pi(b_1)$–σ group.

Analysis of correlation (1) showed that, in complexes of iodine with styrene derivatives, the iodine molecule coordinates with the aromatic system. These complexes show no deviations from the calculated linear dependence for the group of benzene $\pi(b_1)$–σ complexes, and the π system of the aromatic ring of such donors makes a larger contribution to HOMO than does the vinyl fragment. For 1-phenyl-1-propene, we used in calculations the ionization potentials of the more stable *E* isomer. Furthermore, the charge-transfer band in the spectrum of the complex of 1-phenyl-1-propene well fits linear equation (1) with the coefficients *a* and *b* for this group. The specific isomer of this donor was not indicated in [11].

The complex of iodine with 1,3-dimethoxybenzene cannot be included in the group of benzene $\pi(b_1)$–σ complexes, as follows from the first adiabatic ionization potential of this donor and the wavelength of the maximum of the charge-transfer band of its complex (λ_{max} 352 nm [11]). The first adiabatic ionization potential of this donor can be estimated at 7.94 eV from the first vertical ionization potential (IP_{1v} 8.14 eV [7]) and the difference between the vertical and adiabatic ionization potenitals of related compounds (hydroxy and methoxy derivatives of benzene), 0.20 eV [28]. This complex shows a major deviation from the linear dependence obtained for the benzene $\pi(b_1)$–σ group. If the complex were included in this group, the expected position of its charge-transfer band would be 365 nm. The concerted mesomeric effect of two methoxy groups results in a high π-electron density on the C^2, C^4, and C^6 atoms of the aromatic ring. As a result, the acceptor can interact locally with one of these atoms, and the structure of the complex will differ in this case from that of the benzene $\pi(b_1)$–σ complexes.

The complex of iodine with iodobenzene cannot be included in this group, although the complexes of the other halobenzenes are included. The iodobenzene molecule has a low first adiabatic ionization potential (8.80 eV [7]). The complex of iodobenzene with iodine has a very high energy of the charge-transfer transition (4.66 eV [11]), strongly deviating from the value expected from correlation (1) for the benzene $\pi(b_1)$–σ complexes. The situation is not improved by using the second ionization potential of iodobenzene. Some published data on the spectra of complexes of fluorobenzenes (e.g., of *o*-, *m*-, and *p*-fluorotoluenes) were not used in the correlation analysis and are not given in Table 1, because they are not confirmed by data of other authors or are indicated as insufficiently reliable by the authors themselves [18, 19].

The second group of benzene complexes, $\pi(a_2)$–σ (Table 1), is smaller. In the electronic spectra, to complexes of this group mainly corresponds the second (short-wave) band. This group includes complexes of iodine with similar [compared to the $\pi(b_1)$–σ group] benzene derivatives, some halobenzene isomers, and diphenyl. In particular, the group includes complexes with 1,4-dimethyl benzene derivatives (*p*-xylene, 1,2,4-trimethylbenzene, 1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene, 1,2,4,5-tetramethylbenzene). The hypsochromic shift of the bands of complexes formed by 1,4-dimethyl benzene derivatives, compared to their isomers, is characteristic of the complexes not onlywith iodine, but also with other acceptors [29]. The σ orbital of the acceptor in complexes of this group interacts with the $\pi(a_2)$ orbital of the donor molecule (HOMO – 1) having lower energy than HOMO. This orbital of the donor molecules has nodes at the C^1 and C^4 atoms of the aromatic ring. It was suggested previously [30] that the short-wave charge-transfer bands correspond to the transition from HOMO – 1 rather than from HOMO. The selective interaction of the orbital of the acceptor molecule with certain orbitals of the donor molecules of the same type (e.g., π) was discussed in the literature [19, 31] but was not interpreted as occurring in complexes of different configurations.

The satisfactory correlation quality for this group of complexes (even with IP_a) is due to the narrow range of variation of IP of the donor molecules, from 8.90 to 9.62 eV [the range of variation of IP of the donor molecules from the group of the benzene $\pi(b_1)$–σ complexes is wider by a factor of 2.5: from 7.50 to 9.32 eV]; however, in this case also the correlation with IP_a is better than with IP_v.

The necessity of subdividing the complexes of iodine with benzene derivatives into separate groups is due to different values of *a* and *b* in Eqs. (1) for these groups of complexes and to different structures of the orbitals of the donor molecules with which the σ orbital of the acceptor interacts. The correlation (1) for the group of benzene $\pi(a_2)$–σ complexes lies somewhat lower in the energy compared to the correlation (1) for the group of benzene $\pi(b_1)$–σ complexes (in the examined range of IPs of the donors). This fact suggests more favorable interaction of the iodine σ

orbital with the $\pi(a_2)$ orbital of benzene and its derivatives, compared to the interaction with the $\pi(b_1)$ orbitals of these donors. The coefficients *a* of the dependences for the two groups of benzene derivatives are close, but the coefficient *b* of the second dependence is larger. Since the electron is transferred from the donor molecule to the same orbital of the acceptor (lowest unoccupied molecular orbital, LUMO), hν for the transfer from HOMO should be smaller than for the transfer from HOMO – 1. The electron transfer from HOMO – 1 to LUMO + 1 would require still more energy. Although $h\nu$ of the first band is less than $h\nu$ of the second band, the correlation (1) for the second band in the $h\nu$–IP coordinates lies below the correlation for the first band, becaues $IP_1 < IP_2$. If we consider the electronic transitions within the complex of the same structure, all the charge-transfer bands (first and second) should be described by a single correlation of type (1), as discussed in [30]. According to the Koopmans theorem [5], the ionization potential is proportional to the energy of the level from which the electron is removed. Equation (1) gives a linear correlation of the ionization potential with the energy of the charge-transfer transition. Hence, Eq. (1) should linearly relate $h\nu_i$ to IP_j at $i = j$. This is the case for tetracyanoethylene complexes [32] but is not confirmed in this study for complexes of iodine with aromatic donors.

This fact can be accounted for only by structural differences between the benzene $\pi(b_1)$–σ and $\pi(a_2)$–σ complexes. In the first group, the acceptor apparently coordinates with either the C^6–C^1–C^2 or C^3–C^4–C^5 fragment of the aromatic ring. In the second group, the coordination site is the C^2–C^3 or C^5–C^6 bond. The latter assumption is confirmed by published data [33] on the complex of iodine with pyrene, in which the acceptor molecule coordinates at the center of one of the C–C bonds of the pyrene molecule.

It is also remarkable that, among the two degenerate $\pi(b_1)$ and $\pi(a_2)$ orbitals of benzene, the observed band of the benzene–iodine complex corresponds to the transition from the $\pi(a_2)$ orbital. The calculated energy of the charge-transfer transition from the $\pi(b_1)$ orbital is ~4.48 eV (276 nm). There are indications in the literature that the benzene–iodine complex, indeed, exhibits short-wave bands assignable to charge-transfer transitions in the gas phase (268 [34] or 282 nm [35]) and in CCl_4 solution (260 nm [9]). However, these values are poorly consistent with the values calculated for the group of benzene $\pi(b_1)$–σ complexes. The observed deviations may be due to a large error in determination of the maximum of the charge-transfer band of the complex at the wavelength close to that of a strong intrinsic absorption band of benzene (255 nm). The other cause of the deviations may be nonlinearity of correlation (2) [1, 3]:

$$h\nu = f(\mathrm{IP}). \tag{2}$$

The assignment of complexes of iodine with hexasubstituted and 1,3,5-substituted benzenes to different groups of complexes deserves particular consideration. The molecules of such donors have two degenerate HOMOs of the $\pi(b_1)$ and $\pi(a_2)$ types [5]. The complexes of such derivatives containing CH_3 and Br substituents belong to the group of benzene $\pi(b_1)$–σ complexes, and with the H, F, and Cl substituents the complexes belong to the $\pi(a_2)$–σ group.

Complexes of hexamethylbenzene and 1,3,5-trimethylbenzene with iodine belong to the group of benzene $\pi(b_1)$–σ complexes. The wavelengths of the maxima of the charge-transfer bands, calculated for the complexes of these two donors by Eq. (1) on the assumption of the $\pi(a_2)$–σ group, are 400 and 350 nm, respectively. Such bands are not reported in the literature, although these complexes have been thoroughly studied in many solvents [10, 11–14]. The complex of iodine with 1,3,5-tribromobenzene, according to our analysis of its spectral properties and ionization potential of the donor component, also belongs to the benzene $\pi(b_1)$–σ group. The complexes of iodine with hexachlorobenzene and 1,3,5-trifluorobenzene belong to the group of benzene $\pi(a_2)$–σ complexes. In this case, the σ orbital of the acceptor preferentially interacts with the $\pi(a_2)$ orbitals of the donors. The calculated position of the bands of these complexes at electron transfer from the $\pi(b_1)$ level is 291 and 258 nm, respectively, and such bands were revealed neither in [18] nor in our study.

The acceptor substituents (F and Cl in hexasubstituted and 1,3,5-trisubstituted benzenes) favor the interaction of iodine with the $\pi(a_2)$-type molecular orbital. Remarkably, hydrogen exerts an σ-acceptor effect. Donor substituents (alkyls in related hexa- and 1,3,5-trisubstituted benzenes) favor interaction of iodine with a $\pi(b_1)$-type molecular orbital. The same is true for the complex of iodine with 1,3,5-tribromobenzene. Barkhash *et al*. [36] discuss the inversion of the inductive effects of electronegative elements: halogens and chalcogens. The σ-acceptor effect of the F and Cl atoms changes for the σ-donor effect of the Br and I atoms. Therefore, apparently, the above-discussed iodobenzene complex lies out of correlation (1) (the iodine substituent exerts a donor effect both through the system of σ bonds and through space, similar to the effect of nitrogen in complexes of iodine with aromatic amines).

A special remark concerning the complex of iodine with diphenyl should be given. With respect to the second band, it belongs to the group of benzene $\pi(a_2)$–σ complexes. The $\pi(a_2)$ orbital of diphenyl is characterized by the lack of conjugation between the aromatic rings, i.e., each of the two independent $\pi(a_2)$ orbitals of the diphenyl rings interacts with the iodine σ orbital similarly to the $\pi(a_2)$ orbital of the benzene molecule. The first band of this complex (λ_{max} 340 nm [21]) apprecipably deviates from the correlation (1) for the group of benzene $\pi(b_1)$–σ complexes: The calculated value is 365 nm. The first band corresponds to the ionization of the $\pi(b_1)$ level of diphenyl with the conjugation between the rings; this level is not a full analog of the $\pi(b_1)$ level of benzene. Hence, the long-wave band in the spectrum of the diphenyl–iodine complex corresponds to a particular group of complexes of iodine with diphenyl derivatives. A similar pattern was observed with *sym*-trinitrobenzene complexes [25].

Donors with bulky substituents form complexes whose charge-transfer bands are shifted hypsochromically relative to the complexes of the donors having no bulky substituents. A single bulky substituent produces no steric hindrance to the complexation. For example, the bands in the spectra of the iodine complexes with *tert*-butylbenzene and isopropylbenzene well fit linear equation (1) for the group of benzene $\pi(b_1)$–σ complexes. The complexes of benzene derivatives containing two, three, or more bulky substituents (including even the ethyl derivatives) do not fit Eq. (1) for any of the groups of complexes. Such complexes were assigned to a particular group of sterically hindered benzene $\pi(b_1)$–σ complexes. Correlation equation (1) for this group of donors was obtained only with the vertical ionization potentials of the donors. The quality of this correlation is poor, which may be caused both by the nonadditive effect of bulky substituents in molecules of different donors on the spectral properties of the complexes, by the use of IP_v, and by the small sample size. The effects of bulky substituents on the spectral properties of complexes of *sym*-trinitrobenzene and other acceptors are known and are accounted for by the features of the steric structure of the complexes [4, 31].

Using the correlation equations obtained (Table 2) and data on the positions of the charge-transfer bands in the spectra of some complexes, we calculated the adiabatic ionization potentials of donor molecules (Table 1). The calculated adiabatic ionization potentials virtually coincide with the experimental vertical ionization potentials for alkylbenzenes (it is known [5] that, for alkylbenzenes, $IP_{1a} = IP_{1v}$), halobenzenes ($IP_{1a} = IP_{1v}$), and anisole ($IP_{2a} = IP_{2v}$). For these compounds, the deviations of the calculated IPs from the experimental values do not exceed the typical error of IP determination by photoelectron spectroscopy (0.03 eV). The calculated ionization potentials of the donors were not used in the correlation analysis with Eq. (1).

EXPERIMENTAL

Iodine was of analytically pure grade; its concentration in solutions of complexes was 0.05 M.

The following commercially available donors were used: toluene (chemically pure for spectroscopy grade), isopropylbenzene (analytically pure grade, vacuum-distilled), *tert*-butylbenzene (analytically pure grade, vacuum-distilled), *p*-xylene (analytically pure grade), 1,2,4-trimethylbenzene (analytically pure grade), 1,2,4,5-tetramethylbenzene (analytically pure grade), tetralin (analytically pure grade, vacuum-distilled), phenol (analytically pure grade, vacuum-distilled), 2,6-di-*tert*-butyl-4-methylphenol (analytically pure grade), and hexachlorobenzene (analytically pure grade). The concentrations of the donor components in the solutions of the complexes exceeded the iodine concentration by a factor of 3–10.

The UV spectra of molecular complexes were taken from solution in CCl_4 (ultrapure grade) on an SF-46 spectrophotometer at room temperature in 1-cm quartz cells at 2-nm steps. The correlation analysis was performed by methods described previously [4, 25, 28].

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