Electronic absorption spectra of charge-transfer complexes and effects of substituents in radical cations

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The effects of X substituents on the energies of charge-transfer bands $h\nu_{CT}$ in electronic absorption spectra of charge-transfer complexes of π-, n-, or σ-donors (DX) with π- or σ-acceptors (A) as well as on the ionization potentials I_D of individual DX molecules are described by the equation $h\nu_{CT}(I_D) = a + b\sigma_I + c\sigma_R^+ + d\sigma_\alpha$. When DX and A are fixed, the inductive ($b\sigma_I$), resonance ($c\sigma_R^+$), and polarization ($d\sigma_\alpha$) contributions to $h\nu_{CT}$ and I_D are virtually identical. The electronic structure of the $D^{\cdot+}X$ donor component of the compact $[A^{\cdot-}, D^{\cdot+}X]$ radical-ionic pair in a solution is similar to that of the radical cation generated upon photoionization of the individual DX molecule in the gaseous phase.

Key words: charge-transfer complexes, ionization potentials, radical cations, inductive effect, conjugation, polarizability of substituents.

Electronic absorption spectroscopy of charge-transfer complexes formed by neutral DX and A molecules (electron donors and electron acceptors, respectively) has long been used in studies of the effects of the X substituents bound to the donor center D (see, for example, Refs. 1—8).

The contribution of the A...DX structure with a van der Waals interaction prevails in the ground electronic state of charge-transfer complexes [A, DX], whereas the contribution of the $A^{\cdot-}$—$D^{\cdot+}X$ radical-ionic structure with complete electron transfer from DX to A is dominant in the excited state $[A^{\cdot-}, D^{\cdot+}X]$.[1] The energy $h\nu_{CT}$ of electron transition corresponding to a charge-transfer band in absorption spectra of charge-transfer complexes is related to the ionization potential (IP) of the DX donor by the following equation

$$h\nu_{CT} = aI_D - b. \qquad (1)$$

The validity of linear dependence (1) was confirmed many times by comparing the I_D and $h\nu_{CT}$ values for complexes containing diversified DX and A molecules.[1,2,7,8]

Recently, we have examined the effect of the X substituents on the vertical ionization potentials I_D of the molecules of the $R_\pi X$ (R_π is an aromatic or heteroaromatic ring; a double or triple bond)[9,10] and SX_2 series.[11] The predominant localization of the highest occupied molecular orbital (HOMO) on the R_π fragment or on the S atom and, consequently, the formation of radical cations of only two types, *viz.*, $R_\pi^{\cdot+}X$ and $S^{\cdot+}X_2$, on removal of an electron from the HOMO was provided by choosing particular X substituents. In the Hammett—Taft correlation approach, the effects of the X substituents on the ionization potentials are described by the following equations:

$$I_D = c + d\sigma_I + k\sigma_R^+ + l\sigma_\alpha \qquad (2)$$

and

$$I_D = c + m\sigma_p^+ + l\sigma_\alpha. \qquad (3)$$

where *c* is the ionization potential I_D when X = H, σ_I is the universal induction constant of the X substituent, σ_R^+ its resonance parameter, characterizing conjugation in the presence of a positive charge on the radical-cationic center, and σ_α is the polarization constant; $\sigma_p^+ = \sigma_I + \sigma_R^+$. The *d*, *k*, *l*, and *m* coefficients depend on the type of the radical-cationic center.[9—11]

It is of prime importance that the effect of the X substituent on the IP is not reduced to the inductive effect and conjugation. A dipole is induced in the polarizable X substituents under the effect of the positive charge localized on the radical cations $R_\pi^{\cdot+}X$ and $S^{\cdot+}X_2$. In this case, the charge is stabilized by the cation-dipole electrostatic attraction. In the Hammett—Taft approach, this attraction is quantitatively characterized by the σ_α constant.[12] The inductive ($d\sigma_I$), resonance ($k\sigma_R^+$), and polarization ($l\sigma_\alpha$) contributions to the total change in the I_D value under the effect of the X substituent (Eq. (2)) are comparable.[9—11]

The existence of linear dependence (1) between $h\nu_{CT}$ and I_D suggests that the effect of the X substituents on $h\nu_{CT}$ is also not reduced to the inductive effect and conjugation. In spite of this, the polarization contribution to $h\nu_{CT}$, as far as we know, has not yet been taken into account. The aim of this work is to reveal the quantitative relationship between the energy of the charge-transfer bands $h\nu_{CT}$ and the properties of the substituents in charge-transfer complexes containing donors and acceptors of different nature with the use of a procedure developed for the analysis of IP.

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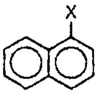
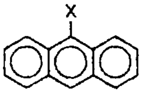
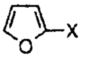
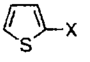
Calculation procedure

The energies $h\nu_{CT}$ of electron transitions corresponding to the charge-transfer bands in the spectra of 13 series of charge-transfer complexes containing DX and A molecules were examined (Table 1). In studies of the effect of the X substituents on $h\nu_{CT}$, it is necessary that the acceptor molecule A (tetracyanoethylene (TCE), trinitrobenzene, hexacyanobenzene, or iodine) and the type of the donor center D in each series *I—XIII* should be the same. The highest occupied MOs of all DX molecules (except for X = H) consist of the orbitals of the subsystems D and X. The character of the donor center D can be considered as typical if its orbitals make a predominant contribution to the HOMO of the DX system. Because of this, a sample in each series *I—XIII* involves only DX molecules for which the predominant contribution of the orbitals of the D subsystem to the HOMO has been established previously by several independent methods (photoelectron spectroscopy, quantum-chemical calculations, and studies of the spectra of charge-transfer complexes).[2–23] In series *I—VII* and *XII*, D is an aromatic ring; in *VIII*, D is the σ Si—Si bond; in *IX—XI*, D is a triple bond; and in *XIII*, D is the sulfur atom. Consequently, according to a standard classification,[1,2] the charge-transfer complexes of series *I—VII* and *XII* belong to the π,π type, and the complexes of series *VIII*, *IX—XI*, and *XIII* belong to the σ,π, π,σ, and n,π types, respectively.

For series *I—VIII*, we analyzed the ionization potentials I_D of the individual DX molecules along with the $h\nu_{CT}$ values (Tables 2 and 3). This makes it possible to compare the effects of the X substituents on two independent characteristics, *viz.*, on $h\nu_{CT}$ and I_D, and thereby to compare the effects of the X substituents in the radical-cationic $D^{\cdot +}X$ species formed in the excited state of the charge-transition complexes $[A^{\cdot -}, D^{\cdot +}X]$ in solutions as well as in those formed upon photoionization of the individual DX molecules in the gaseous phase (conditions of measurements of I_D by photoelectron spectroscopy[10,21]). For the DX donor molecules of series *IX—XIII*, complete sets of the I_D values, which could be related to the $h\nu_{CT}$ values in the spectra of charge-transfer complexes formed from DX and A, are lacking. Hence, only the effect of the X substituents on the $h\nu_{CT}$ values was considered for the latter series (Table 4). In spite of this, series *IX—XIII* attract interest from the standpoint of an increase in the number of the studied types of DX and A compounds and elucidation of the generality of the concepts of the effects exhibited by the X substituents in the $D^{\cdot +}X$ radical cations, which are being developed based on the data for series *I—VIII*.

The main purposes of this work were as follows: verification of the validity of Eq. (1) for series *I—VIII*; analysis of the possibility of representing $h\nu_{CT}$ as a function of two arguments (σ_I and σ_R^+) and examination of the validity of introduction of the third argument, *viz.*, σ_α; separation of the effect of the X substituents on $h\nu_{CT}$ and I_D into components; quantitative comparison of the effects of the X substituents in the radical-cationic forms $D^{\cdot +}X$ prepared from individual molecules (gaseous phase) and those in charge-transfer complexes (solutions). Correlation equations were found with the use of the standard STATGRAPHICS 3.0 program package on a PC/AT 286 computer. The data were processed by the least-squares method at the 95% confidence level.

Table 1. Series of the charge-transfer complexes under study

Series	Donor DX	Acceptor A	Solvent
I	C_6H_5X	$(NC)_2C{\equiv}C(CN)_2$	CH_2Cl_2
II	C_6H_5X	$1,3,5\text{-}C_6H_3(NO_2)_3$	CCl_4
III	C_6H_5X	$C_6(CN)_6$	DX*
IV		$(NC)_2C{=}C(CN)_2$	CH_2Cl_2
V		$(NC)_2C{=}C(CN)_2$	CH_2Cl_2
VI		$(NC)_2C{=}C(CN)_2$	CH_2Cl_2
VII		$(NC)_2C{=}C(CN)_2$	CH_2Cl_2
VIII	X_3SiSiX_3	$(NC)_2C{=}C(CN)_2$	CH_2Cl_2
IX	$Me_3CC{\equiv}CX$	I_2	CCl_4
X	$Me_3SiC{\equiv}CX$	I_2	CCl_4
XI	$Me_3GeC{\equiv}CX$	I_2	CCl_4
XII	$1,4\text{-}Me_2NC_6H_4X$	$1,3,5\text{-}C_6H_3(NO_2)_3$	$CHCl_3$
XIII	$1,4\text{-}ClSC_6H_4X$	$(NC)_2C{=}C(CN)_2$	CH_2Cl_2

* CH_2Cl_2 for the charge-transfer complexes with the participation of DX = $C_6H_5C_6H_5$ (see Table 2, compound 5).

Results and Discussion

For charge-transfer complexes of series *I—VIII*, the linear dependences between $h\nu_{CT}$ and I_D are fulfilled (Table 5). For the ranges of the changes in the $h\nu_{CT}$ and I_D values given in Table 2, the straight lines described by Eqs. (4), (7), and (8) virtually coincide with that described by the equation

$$h\nu_{CT} = 0.83I_D - 4.42, \qquad (12)$$

for charge-transfer complexes of various benzene derivatives[23] with TCE. The straight lines described by Eqs. (9) and (10) coincide with that described by the equation

$$h\nu_{CT} = 0.819I_D - 4.46 \qquad (13)$$

for charge-transfer complexes of derivatives of ethylene, acetylene, and heteroaromatic π donors[23] with TCE. Straight line (11) is shifted with respect to lines (12) and (13), which are nearly parallel to line (11), toward higher $h\nu_{CT}$ values. This is indicative of steric hindrances upon formation of charge-transfer complexes of X_3SiSiX_3 with TCE.[23] These hindrances result in an increase in the length of the donor-acceptor bond as well as in an increase in the $h\nu_{CT}$ value. The fact that straight lines (11) and (12) are nearly parallel to one another indicates that the steric factors in compounds of series *VIII* are nearly identical. Therefore, Eq. (1) is valid for all compounds of series *I—VIII* under study.

Let as consider the effect of the X substituents on the energies of the charge-transfer bands $h\nu_{CT}$. Assume that only two parameters (inductive σ_I and resonance σ_R^+) of the X substituents affect the $h\nu_{CT}$ value. Calculations

Table 2. Energies of electron transfer ($h\nu_{CT}$/eV) in the charge-transfer complexes, the ionization potentials (I_D/eV), and the σ parameters of the X substituents for series *I—VII*

Compound*	X	*I*		*II*		*III*		*IV*		*V*		*VI*		*VII*		σ_I	σ_R^+	σ_α
		$h\nu_{CT}$	I_D[9]	$h\nu_{CT}$[15]	I_D[15]	$h\nu_{CT}$[16]	I_D[15]	$h\nu_{CT}$	I_D[10]	$h\nu_{CT}$[7]	I_D[7,10]	$h\nu_{CT}$[8]	I_D[10]	$h\nu_{CT}$[19]	I_D[10]			
1	H	3.22[7]	9.24	4.38	9.24	3.55	9.24	2.25[7]	8.12	1.73	7.43	2.76	8.89	2.77	8.87	0	0	0
2	Me	2.91[7]	8.72	4.07	8.72	3.25	8.72	2.11[7]	7.85	1.55	7.25	2.39	8.37	2.48	8.43	−0.05	−0.26	−0.35
3	Pr^i	2.99[3]	8.73	—	—	—	—	—	—	—	—	—	—	—	—	−0.03	−0.25	−0.62
4	Bu^t	2.74[7]	8.74	—	—	—	—	—	—	—	—	2.38	8.19	2.45	8.32	−0.07	−0.19	−0.75
5	Ph	—	—	3.55	8.32	2.53	8.32	—	—	1.59	7.18	—	—	—	—	0.12	−0.30	−0.81
6	CH_2OH	—	—	—	—	—	—	—	—	1.73	7.47	—	—	—	—	0.03	−0.07	−0.36
7	CH_2Cl	3.26[13]	9.27	—	—	—	—	—	—	—	—	—	—	—	—	0.13	−0.14	−0.54
8	CH_2Br	3.25[3]	9.23	—	—	—	—	—	—	—	—	—	—	—	—	0.14	−0.12	−0.61
9	NH_2	2.10[7]	8.05	3.10	8.05	—	—	1.81[17]	7.48	—	—	—	—	—	—	0.08	−1.38	−0.16
10	NHMe	1.94[7]	7.65	—	—	—	—	—	—	—	—	—	—	—	—	−0.03	−1.78	−0.30
11	NMe_2	1.84[7]	7.45	2.56	7.45	1.88	7.45	—	—	—	—	—	—	—	—	0.15	−1.85	−0.44
12	NEt_2	—	—	2.40	7.20	—	—	—	—	—	—	—	—	—	—	0.01	−2.08	−0.56
13	OH	2.54[7]	8.56	3.53	8.56	—	—	1.96[17]	7.78	—	—	—	—	—	—	0.33	−1.25	−0.03
14	OMe	2.46[7]	8.42	3.52	8.42	2.72	8.42	1.88[17]	7.70	1.65	7.21	—	—	2.16	8.18	0.29	−1.07	−0.17
15	F	3.45[13]	9.20	4.33	9.20	—	—	—	—	—	—	—	—	—	—	0.45	−0.52	0.13
16	Cl	3.08[7]	9.07	—	—	—	—	2.28[17]	8.13	1.74	7.46	—	—	2.69	8.89	0.42	−0.31	−0.43
17	Br	3.05[7]	9.04	—	—	—	—	2.27[17]	8.09	1.74	7.47	—	—	2.64	8.82	0.45	−0.30	−0.59
18	CN	3.83[7]	9.71	—	—	—	—	—	—	2.01	7.82	—	—	—	—	0.51	0.15	−0.46
19	CHO	—	—	—	—	—	—	—	—	1.90	7.69	3.10	9.21	—	—	0.33	0.40	−0.46
20	COOH	3.35[7]	9.60	—	—	—	—	—	—	—	—	—	—	—	—	0.34	0.08	−0.34
21	COOMe	—	—	—	—	—	—	—	—	1.84	7.48	—	—	—	—	0.34	0.14	−0.49
22	CF_3	3.78[13]	9.86	—	—	—	—	—	—	—	—	—	—	—	—	0.38	0.23	−0.25
23	NO_2	—	—	—	—	—	—	—	—	2.03	7.88	—	—	—	—	0.65	0.14	−0.26
24	SiH_3	3.22[7]	9.18	—	—	—	—	2.24[18]	8.02	—	—	2.58	8.75	—	—	−0.04	0.03	−0.59
25	$SiHMe_2$	—	—	—	—	—	—	—	—	—	—	2.55	8.62	—	—	−0.12	0.02	−0.68
26	$SiMe_3$	2.92[5]	8.94	—	—	—	—	2.15[18]	7.92	—	—	2.53	8.48	2.54	8.64	−0.15	0.02	−0.72
27	$Si(OEt)_3$	—	—	—	—	—	—	—	—	—	—	2.67	8.66	—	—	−0.10	0.11	−0.63
28	$GeMe_3$	2.90[5]	8.95	—	—	—	—	2.12[18]	7.88	—	—	2.48	8.47	2.52	8.52	−0.11	−0.11	−0.60
29	$SnMe_3$	2.78[5]	8.75	—	—	—	—	2.11[18]	7.87	—	—	2.36	8.33	2.49	8.49	−0.13	−0.21	−0.60
30	$PbMe_3$	2.60[5]	8.54	—	—	—	—	—	—	—	—	—	—	2.47	8.46	−0.12	−0.26	−0.60
31	CH_2SiMe_3	2.50[14]	8.42	—	—	—	—	1.95[18]	7.67	—	—	2.26	8.15	—	—	−0.05	−0.49	−0.66
32	$C(SiMe_3)_3$	2.34[14]	8.10	—	—	—	—	—	—	—	—	—	—	—	—	−0.05	−0.63	−1.28
33	CH_2GeMe_3	2.43[14]	8.40	—	—	—	—	1.90[18]	7.61	—	—	—	—	—	—	−0.04	−0.59	−0.61
34	CH_2SnMe_3	2.17[14]	8.21	—	—	—	—	1.72[18]	7.40	—	—	—	—	—	—	−0.05	−0.76	−0.61

Note. The σ_I and σ_α values for all substituents and the σ_R^+ values for the organic and organometallic substituents for series *I* were taken from the literature.[9,12] The σ_R^+ parameters for the organometallic substituents for series *IV*, *VI*, and *VII* were taken from the literature.[10]

* Here and in Tables 3 and 4, different arbitrary numbering schemes of the compounds are used.

Table 3. Energies of electron transfer ($h\nu_{CT}$/eV) in the charge-transfer complexes, the ionization potentials (I_D/eV), and the sums of the σ parameters of the X substituents in X_3SiSiX_3 (series *VIII*)

Compound*	$h\nu_{CT}$[20]	I_D	$\Sigma\sigma_I$	$\Sigma\sigma_R^+$	$\Sigma\sigma_\alpha$
$Me_3SiSiMe_3$ (**1**)	2.95	8.69[21]	−0.30	−1.56	−2.10
$Et_3SiSiEt_3$ (**2**)	2.69	8.39[21]	−0.30	−1.50	−2.94
$BuMe_2SiSiMe_3$ (**3**)	2.89	8.57[20]	−0.30	−1.55	−2.32
$BuMe_2SiSiMe_2Bu$ (**4**)	2.80	8.45[20]	−0.30	−1.54	−2.54
$Me_3SiSiMe_2OEt$ (**5**)	3.03	8.75[20]	0.01	−2.37	−1.98
$Me_3SiSiMe_2Cl$ (**6**)	3.28	9.08[20]	0.17	−1.61	−2.18
$BuMe_2SiSiMe_2Cl$ (**7**)	3.26	9.05[20]	0.17	−1.60	−2.40
$Me_3SiSiMeCl_2$ (**8**)	3.57	9.48[20]	0.64	−1.66	−2.26
$ClMe_2SiSiMe_2Cl$ (**9**)	3.60	9.48[20]	0.64	−1.66	−2.26
$Me_3SiSiMe_2SiMe_3$ (**10**)	2.58	8.19[21]	−0.40	−1.28	−2.47
Me_3SiMe_2Si— —$SiMe_2SiMe_3$ (**11**)	2.38	7.98[21]	−0.50	−1.00	−2.84

Note. See the note in Table 2.

* See the reference in Table 2.

Table 4. Energies of electron transfer ($h\nu_{CT}$/eV) in the spectra of the charge-transfer complexes (series *IX—XIII*)

Compound*	X	*IX*	*X*	*XI*	*XII*	*XIII*
1	H	—	—	—	2.52	2.32
2	Me	4.28	4.45	4.25	2.42	2.23
3	Bu^t	4.22	4.34	4.25	—	—
4	CH_2OH	—	—	—	2.51	—
5	CH_2Cl	4.59	4.62	4.52	—	—
6	NH_2	—	—	—	2.21	—
7	OMe	—	—	—	2.35	2.16
8	Cl	4.28	4.43	4.46	2.57	2.31
9	Br	4.22	4.34	4.43	2.56	—
10	NO_2	—	—	—	—	2.43

Note. See the note in Table 2. Series *IX—XI*, *XII*, *XIII* according to literature data,[4,22,6] respectively.

* See the reference in Table 2.

Table 5. The a and b coefficients for the equation $h\nu_{\mathrm{CT}} = aI_{\mathrm{D}} - b$, the standard deviations S_a and S_b, the standard errors of approximation S_Y, the correlation coefficients r, and the size of the sample n

Series	a	b	S_a	S_b	S_Y	r	n	Equation
I	0.87	4.77	0.04	0.34	0.11	0.977	26	(4)
II	1.00	4.88	0.06	0.49	0.12	0.988	9	(5)
III	0.98	5.43	0.11	0.92	0.14	0.982	5	(6)
IV	0.78	4.04	0.04	0.34	0.04	0.982	14	(7)
V	0.66	3.14	0.06	0.42	0.04	0.968	11	(8)
VI	0.72	3.57	0.06	0.54	0.06	0.967	11	(9)
VII	0.65	3.01	0.09	0.74	0.06	0.934	10	(10)
VIII	0.80	3.96	0.01	0.12	0.02	0.999	11	(11)

demonstrated that under this assumption, the correlation coefficient r in the two-parameter relations

$$h\nu_{\mathrm{CT}} = c + d\sigma_{\mathrm{I}} + k\sigma_{\mathrm{R}}^{+} \quad (14)$$

depends substantially on the type of the series. For example, a good correlation dependence ($r = 0.996$) is observed for series *XII*, whereas the correlation is absent completely ($r = 0.000$) for series *X*. For the remaining series, the correlation coefficients are intermediate between the r values for series *X* and *XII*.

Let us further assume that the energy $h\nu_{\mathrm{CT}}$, like the ionization potential I_{D}, depends on the polarization parameter σ_α of the X substituent (Table 6).

On going from two-parameter Eq. (14) to Eqs. (15)—(35), the statistical characteristics of the correlation equations are substantially improved in all cases. Thus the correlation coefficient r increases, while the standard deviations of the coefficients c, d, k, and l and the standard error of the approximation S_Y decrease. This situation is most pronounced for series *X* and *XII*. Thus, the correlation coefficient r for compounds of series *X* increases from 0.000 to 0.994. For series *XII*, the coefficient r, which is very high (0.996) even in the case of Eq. (14), increases still further (see Table 6).

From Eqs. (15)—(35) it follows that, like the ionization potentials I_{D} of the individual DX molecules (series *I—VIII*), the energies of the charge-transfer bands $h\nu_{\mathrm{CT}}$ in the electronic absorption spectra of charge-transfer complexes formed by the DX and A molecules (series *I—XIII*) depend on the inductive, resonance, and polarization effects of the X substituents. The contributions of $d\sigma_{\mathrm{I}}$, $k\sigma_{\mathrm{R}}^{+}$, and $l\sigma_\alpha$ to the total changes in the $h\nu_{\mathrm{CT}}$ and I_{D} values under the effect of the X substituents depend on the series (Table 7). Series *I—VIII* each allows one to compare the above-mentioned contributions to $h\nu_{\mathrm{CT}}$ and I_{D}. The data given in Table 7 indicate that the corresponding contributions to $h\nu_{\mathrm{CT}}$ and I_{D} surprisingly coincide within the experimental error. (The largest discrepancy between the inductive contributions to $h\nu_{\mathrm{CT}}$ and I_{D} is observed for series *III*.)

The fact that the contributions to the $h\nu_{\mathrm{CT}}$ and I_{D} values are equal in each series *I—VIII* signifies that the effects of the X substituents in the radical-cationic forms of two types are identical. The $\mathrm{D^{\cdot +}X}$ radical cations of the first type exist in the gaseous phase and are formed upon photoionization of the individual DX molecules. In this case, an electron is removed from the HOMO

Table 6. The c, d, k, and l coefficients for the equations $h\nu_{\mathrm{CT}}(I_{\mathrm{D}}) = c + d\sigma_{\mathrm{I}} + k\sigma_{\mathrm{R}}^{+} + l\sigma_\alpha$, the standard deviations S_c, S_d, S_k, and S_l, the standard errors of approximation S_Y, the correlation coefficients r, and the size of the sample n

Series	Property	c	d	k	l	S_c	S_d	S_k	S_l	S_Y	r	n	Equation
I	$h\nu_{\mathrm{CT}}$	3.28	0.86	0.81	0.36	0.08	0.15	0.05	0.12	0.14	0.963	26	(15)
	I_{D}	9.33	0.86	0.94	0.46	0.06	0.12	0.04	0.10	0.12	0.981	26	(16)
II	$h\nu_{\mathrm{CT}}$	4.45	0.34	0.82	0.78	0.08	0.26	0.05	0.15	0.11	0.989	9	(17)
	I_{D}	9.25	0.55	0.75	0.95	0.05	0.16	0.03	0.09	0.06	0.996	9	(18)
III	$h\nu_{\mathrm{CT}}$	3.64	0.00	0.70	1.03	0.11	0.00	0.09	0.22	0.13	0.979	5	(19)
	I_{D}	9.26	0.55	0.80	0.94	0.03	0.16	0.03	0.06	0.03	0.999	5	(20)
IV	$h\nu_{\mathrm{CT}}$	2.28	0.40	0.39	0.14	0.03	0.06	0.02	0.05	0.04	0.977	14	(21)
	I_{D}	8.14	0.59	0.50	0.26	0.03	0.05	0.02	0.05	0.04	0.988	14	(22)
V	$h\nu_{\mathrm{CT}}$	1.75	0.49	0.22	0.20	0.04	0.07	0.04	0.07	0.05	0.949	11	(23)
	I_{D}	7.48	0.64	0.38	0.31	0.06	0.11	0.06	0.11	0.08	0.945	11	(24)
VI	$h\nu_{\mathrm{CT}}$	2.73	0.73	0.69	0.34	0.05	0.17	0.09	0.09	0.06	0.969	11	(25)
	I_{D}	8.89	0.64	1.05	0.65	0.02	0.08	0.04	0.04	0.03	0.996	11	(26)
VII	$h\nu_{\mathrm{CT}}$	2.75	0.57	0.62	0.29	0.04	0.09	0.06	0.07	0.05	0.957	10	(27)
	I_{D}	8.87	1.05	0.87	0.41	0.01	0.03	0.02	0.02	0.02	0.998	10	(28)
VIII	$h\nu_{\mathrm{CT}}$	3.69	0.84	0.00	0.27	0.03	0.08	0.00	0.11	0.09	0.971	11	(29)
	I_{D}	9.48	1.08	0.00	0.29	0.35	0.11	0.00	0.15	0.12	0.970	11	(30)
IX	$h\nu_{\mathrm{CT}}$	5.30	0.43	2.97	0.65	0.00	0.00	0.01	0.00	0.00	1.000	5	(31)
X	$h\nu_{\mathrm{CT}}$	5.21	0.25	2.02	0.63	0.04	0.03	0.12	0.05	0.01	0.994	5	(32)
XI	$h\nu_{\mathrm{CT}}$	4.83	0.65	1.71	0.29	0.05	0.04	0.15	0.06	0.02	0.992	5	(33)
XII	$h\nu_{\mathrm{CT}}$	2.52	0.32	0.24	0.05	0.01	0.03	0.01	0.03	0.01	0.997	7	(34)
XIII	$h\nu_{\mathrm{CT}}$	2.32	0.17	0.18	0.07	0.01	0.02	0.01	0.04	0.01	0.993	5	(35)

Table 7. Inductive ($d\sigma_I$), resonance ($k\sigma_R{}^+$), and polarization ($l\sigma_\sigma$) contributions (%) to the total changes in $h\nu_{CT}$ and I_D under the effect of the X substituents

Series	Property	$d\sigma_I$	$k\sigma_R{}^+$	$l\sigma_\alpha$
I	$h\nu_{CT}$	21±4	61±4	18±6
	I_D	18±2	62±3	20±4
II	$h\nu_{CT}$	6±5	66±4	28±5
	I_D	10±3	57±2	33±3
III	$h\nu_{CT}$	0	61±8	39±8
	I_D	8±2	61±2	31±2
IV	$h\nu_{CT}$	27±4	62±3	11±4
	I_D	28±2	57±2	15±3
V	$h\nu_{CT}$	41±6	39±7	20±7
	I_D	36±6	44±7	20±7
VI	$h\nu_{CT}$	33±8	43±6	24±6
	I_D	21±3	46±2	33±2
VII	$h\nu_{CT}$	25±4	59±6	16±4
	I_D	30±1	55±1	15±1
VIII	$h\nu_{CT}$	79±7	0	21±9
	I_D	81±8	0	19±10
IX	$h\nu_{CT}$	22±0	51±0	27±0
X	$h\nu_{CT}$	18±2	47±3	35±3
XI	$h\nu_{CT}$	45±3	39±3	16±3
XII	$h\nu_{CT}$	31±3	63±3	6±3
XIII	$h\nu_{CT}$	32±4	60±3	8±5

localized predominantly on the donor center D. The $D^{\cdot+}X$ radical cations of the second type exist in solutions as fragments of the radical-ionic pairs $[A^{\cdot-}, D^{\cdot+}X]$, which are formed when charge-transfer complexes are transformed from the ground to the excited state. In this case, an electron is transferred from the HOMO of the DX donor to the LUMO of the A acceptor, which are weakly bound together in the ground electronic state [A, DX] of charge-transfer complexes.

The similarity of the radical-cationic forms of two types is attributable to the characteristic features of the excited state $[A^{\cdot-}, D^{\cdot+}X]$ of charge-transfer complexes formed in the course of reversible processes:

$$A + DX \longleftrightarrow [A, DX] \xleftrightarrow{h\nu_{CT}} [A^{\cdot-}, D^{\cdot+}X].$$

Based on the data of pulse picosecond (1 ps = 10^{-12} s) spectroscopy,[24,25] the transformation from the excited to the ground state [A, DX] occurs very rapidly (the rate constant is 10^8—10^{11} s^{-1}) in the "compact" radical-ionic pair $[A^{\cdot-}, D^{\cdot+}X]$ without insertion of the solvent between its components. From the aforesaid, it might be assumed that the cationic component $D^{\cdot+}X$ of the ionic pair $[A^{\cdot-}, D^{\cdot+}X]$ is analogous in electronic structure to the radical cation formed upon photoionization of the individual DX molecule. The similarity of the effects of the substituents in the radical-cationic forms $D^{\cdot+}X$ of two types, *viz.*, those generated from isolated DX molecules and from the ground state [A, DX] of charge-transfer complexes, is circumstantial evidence in support of the above-mentioned suggestion.

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