Tetrahedron. Vol. 31, pp. 2453 to 2456. Pergamon Press 1975. Printed in Great Britain

NEW IONIZATION POTENTIALS FROM CHARGE-TRANSFER SPECTRA[†]

O. B.NAGY,[*] S. DUPIRE and J. B.NAGY[‡]
Université Catholique de Louvain, Laboratoire de Chimie Générale et Organique, Bâtiment Lavoisier, Place Louis Pasteur, 1, B-1348 Louvain-la-Neuve, Belgium

(*Received in UK* 8 *May* 1975; *Accepted for publication* 22 *May* 1975)

Abstract—New ionization potential values are reported for sixteen aromatic molecules. They are obtained from CT spectra of a new electron acceptor, 3,5-dinitro-phthalic anhydride with the aromatic electron donors in 1,2-dichloroethane. The results are correlated with molecular electronic structure using perturbation theory.

According to the theory of weak molecular complexes[1] a direct relationship exists between the CT energy $h\nu_{CT}$ and the ionization potential, I_D, of the donor molecules:

$$h\nu_{CT} = I_D - C_1 + C_2(I_D - C_1)^{-1} \qquad (1)$$

C_1 and C_2 are constants for a series formed by different donors interacting with the same acceptor molecule.

In many cases an empirical relationship

$$h\nu_{CT} = aI_D + b \qquad (2)$$

has been used to fit the experimental data.[2-7] It has been proposed that the smaller the value of a the stronger will be the resonance interaction between the donor and acceptor molecules.[8] Eqn (2) has also been applied to contact CT spectra.[9] It should be noted that the linear eqn (2) is an approximation of the parabolic eqn (1) when a limited range of I_D is considered.

In the present work a new acceptor, the 3,5-dinitrophthalic anhydride (3,5 NPA), is used to determine the unknown ionization potentials of a series of aromatic π donors. The electron affinity of this acceptor ($E_A = 1{\cdot}1$ eV) was established from CT data.[10]

Table 1 contains the CT energies ($\bar{\nu}_{max}$ in kK; with certain donors two maxima were obtained) for complexes of donors with 3,5 NPA in 1,2-dichloroethane at 20°. ([acceptor] $\simeq 1{\cdot}10^{-3} - 3{\cdot}10^{-3}$ mol l^{-1}; [donor] $\simeq 0{\cdot}1 - 1$ mol l^{-1}).

The ionization potentials determined by photoionization are taken from Ref. 11. These I_D values and the corresponding CT energies are very well correlated (Fig. 1) following the linear relationship:

$$h\nu_{max}(\text{eV}) = 0{\cdot}98(\pm 0{\cdot}04)I_D(\text{eV}) - 5{\cdot}06(\pm 0{\cdot}35). \qquad (3)$$

This equation has been used to determine new I_D values by interpolation (Table 1).[§] Their validity was checked with other complexes formed by tetrachlorophthalic anhydride with the same donors in 1,2-dichloroethane.[12] The corresponding linear relationship is:

$$h\nu_{max}(\text{eV}) = 0{\cdot}90(\pm 0{\cdot}05)I_D(\text{eV}) - 3{\cdot}94(\pm 0{\cdot}36). \qquad (4)$$

Since the slope of eqn (3) is very close to unity, the CT stabilization of the complexes in their ground state is very small[¶] and therefore the intercept may be equated to C_1 in eqn (1). According to the theory[1]

$$C_1 \simeq E_A - E_C + W_0 \qquad (5)$$

where E_A is the electron affinity of acceptor, E_C represents the Coulomb interaction energy and W_0 is the stabilization energy of the complex in the ground state by forces other than charge-transfer ones. If $|E_A - E_C| \gg |W_0|$, as it is true for weak complexes, eqn (5) becomes

$$C_1 \simeq E_A - E_C \qquad (6)$$

and we can determine the Coulomb interaction term: $E_C = -3{\cdot}96$ eV. The same value ($-3{\cdot}97$ eV) was already obtained from the relationship $h\nu_{CT}$ vs E_A in the case of complexes formed by acenaphthene (donor) with several cyclic anhydrides (acceptors).[10] This shows again the reliability of the results obtained.

The variation of the new I_D values with molecular electronic structure can be reasonably accounted for by perturbation theory.

The various substituents are considered as perturbations of the corresponding π electronic systems. It is assumed that, to first order, only the Coulomb integral (α_r) of the substituent bearing C atoms (r) is changed by the perturbation (Hückel approximation): $\alpha_r^{\text{perturbed}} = \alpha_r^{\text{unperturbed}} + \delta\alpha_r$. On the other hand the second order perturbation affects essentially the resonance integral ($\delta\beta_{r-x}$) of the carbon-substituent(x)bonds. In Hückel LCAO-MO approximation the perturbations of the jth energy level can be calculated[13] using the following equations:

[†] Part XV of a series, *Charge-transfer complexes in organic chemistry*.

Part XIV: D. Mukana, J. B.Nagy, O. B.Nagy and A. Bruylants, *Bull. Soc. Chim. Belg.* **83**, 201 (1974).

[‡] Present address: Facultés Universitaires de Namur, Institut de Chimie, Rue de Bruxelles, 61, B-5000 Namur, Belgium.

[§] The small difference (of the order of the standard deviation: ±0·02 eV) existing between these values and those reported in Ref. 12 comes from the fact that an inverse relationship (I_D vs $h\nu_{max}$) was used there for the interpolation.

[¶] In the case of similar complexes we have found indeed[10] that the CT in the ground state amounts to about 5% only.

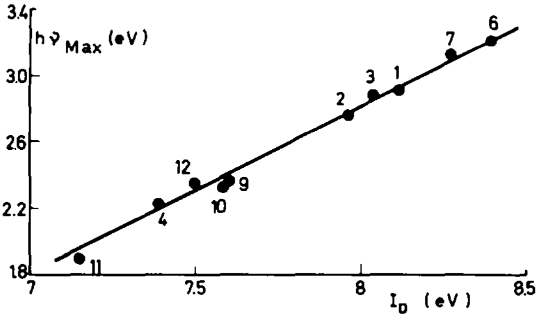

Fig. 1. Variation of the first charge-transfer energies with ionization potential of donors for the complexes donors - 3,5 - dinitrophthalic anhydride in 1,2-dichloroethane at 20 ± 0·1°C.

Table 1. Charge-transfer energies, ionization potentials and electronic structure parameters of donors for complexes donors-3,5-dinitrophthalic anhydride. Solvent: 1,2-dichloroethane; T = 20 ± 0·1°C

N°	Donor	$\bar{\nu}_{max}(I)$[a] (kK)	$\bar{\nu}_{max}(II)$[b] (kK)	$I_D(exp)$[c] (eV)	$I_D(calc)$[g] (eV)	$\delta E_{HO}^{(1)}$ (β)	$\delta E_{HO}^{(2)}$ (β)
1	Naphthalene	23.44	25.50	8.12	-	0	0
2	1-Methylnaphthalene	22.32	25.72	7.96	-	-0.090	-0.015
3	2-Methylnaphthalene	23.30	-	8.04[d]	-	-0.035	-0.006
4	Anthracene	17.92	-	7.38	-	0	0
5	Hexamethylbenzene	-	25.22	7.85	-	-0.50[h]	0
6	1,3,5-Trimethylbenzene	25.87	-	8.39	-	-0.25[h]	0
7	1,2,4-Trimethylbenzene	25.27	-	8.27	-	-0.394[i]	-0.033
8	1,2,4,5-Tetramethylbenzene	-	26.22	8.03	-	-0.50[j]	0
9	1,2-Benzanthracene	19.06	-	7.60[f]	-	-	-
10	Pyrene	18.72	-	7.58	-	-	-
11	Perylene	15.24	-	7.15[f]	-	-	-
12	Coronene	18.96	-	7.50	-	-	-
13	9-Methylanthracene	17.34	-	-	7.36	-0.097	-0.013
14	1,2-Dimethylnaphthalene	21.40	25.70	-	7.87	-0.125	-0.041
15	1,3-Dimethylnaphthalene	21.55	24.50	-	7.89	-0.125	-0.002
16	1,5-Dimethylnaphthalene	21.14	-	-	7.84	-0.181	-0.062
17	2,3-Dimethylnaphthalene	22.09	-	-	7.96	-0.069	0
18	2,6-Dimethylnaphthalene	21.80	-	-	7.92	-0.069	-0.024
19	1,3,7-Trimethylnaphthalene	20.60	25.35	-	7.77	-0.159	-0.001
20	2,3,6-Trimethylnaphthalene	21.42	-	-	7.88	-0.104	-0.006
21	1-Methoxynaphthalene	21.00	-	-	7.82	0.072	-0.131
22	2-Methoxynaphthalene	-	25.80	-	7.80[e]	0.028	-0.050
23	1,7-Dimethoxynaphthalene	19.32	24.02	-	7.60	0.100	-0.019
24	2,6-Dimethoxynaphthalene	19.14	-	-	7.58	0.055	-0.200
25	1-Chloronaphthalene	-	26.30	-	8.05[e]	0.090	-0.021
26	Acenaphthene	20.32	25.37	-	7.73	-	-
27	Ethoxybenzene	25.07	-	-	8.34	0.133[k]	-0.333
28	2-Methylanthracene	17.84	-	-	7.42	-0.024	-0.003

[a] Maximum of the first CT band; [b] Maximum of the second CT band; [c] Ref. 11 photo-ionization values (I_D (benzene) = 9·24 eV); [d] Ref. 7; [e] Estimated values from the curvature of $\bar{\nu}_{max}(II)$ vs I_D; [f] CT value; [g] According to usual statistical analysis the standard deviation of these interpolated values amounts to ±0·02 eV at most; [h] $\Psi_{HO} = \Psi_2 = \Psi_3$; [i] $\Psi_{HO} = \Psi_3' = C_3\Psi_3 + C_2\Psi_2$; [j] $\Psi_{HO} = \Psi_2$; [k] $\Psi_{HO} = \Psi_3$.

1st order perturbation

$$\delta E_j^{(1)} = \langle \Psi_j | H' | \Psi_j \rangle \tag{7}$$

2nd order perturbation

$$\delta E_j^{(2)} = \sum_k \frac{\langle \Psi_j | H' | \Psi_k \rangle^2}{E_j - E_k} \tag{8}$$

Ψ_j and Ψ_k are the zeroth order molecular orbitals of the perturbed (aromatic nucleus) and perturbing (substituent) systems respectively; H′ is the perturbation Hamiltonian operator. Substituting $\Psi_j = \sum_r C_{jr}\phi_r$ and $\Psi_k = \sum_s C_{ks}\phi_s$ (ϕ_i is the ith atomic orbital and C_{ni} is its linear combination coefficient in the nth molecular orbital) into eqns (7) and (8) we obtain the working formulae:

$$\delta E_j^{(1)} = \sum_r C_{jr}^2 \delta\alpha_r \tag{9}$$

and

$$\delta E_j^{(2)} = \sum_k \frac{\left(\sum_{rs} C_{jr} C_{ks} \delta\beta_{rs} \right)^2}{E_j - E_k} \tag{10}$$

where $\delta\alpha_r = \langle \phi_r | H' | \phi_r \rangle$ and $\delta\beta_{rs} = \langle \phi_r | H' | \phi_s \rangle = \langle \phi_s | H' | \phi_r \rangle$. In these equations allowance is made to the presence of several simultaneous perturbations.

The zeroth order energy levels and molecular orbitals as well as the perturbation parameters used in the present work are collected in Table 2. Only the highest occupied MO (Ψ_{HO}) of the perturbed system is considered since according to Koopman's theorem the ionization potential is directly related to the energy of this orbital.

In the case of benzene, the highest occupied level shows a two-fold degeneracy. Therefore a complete two-body problem must be solved using the perturbation Hamiltonian. The results are given in Table 1.†

It can be seen that first order effects are generally much larger than second order ones. Therefore inductive effect (I) is more important than resonance interaction (M) in determining the size and sign of the electronic perturbation. Electron releasing groups (+I, e.g. CH_3–) destabilize while electron attracting ones (–I, e.g. CH_3O–) stabilize the highest occupied molecular orbitals. The resonance effect (+M) is destabilizing in all cases. The relative importance of this latter becomes greater with increasing number of alkoxy substituents. The presence of substituents may decrease the symmetry of a given electronic system. Therefore the perturbation shows a lesser

---

†In the particular case of 1,2,4-trimethylbenzene the perturbation effect of substituents depends surprisingly on the ring numbering. Finally, that numbering was chosen which connects the most closely the positions of substituents to the potential field of ring nuclei.

Table 2. Zeroth order energy levels and molecular orbitals. Perturbation parameters

Electronic system	Energy	Molecular Orbitals	Perturbation parameters (in β units)		References
			1st order: $\delta\alpha_r$	2nd order: $\delta\beta_{r-x}$	
Benzene	$E_2=E_3=\alpha+\beta$	$\Psi_2=0.500(\phi_2+\phi_3)$ $-0.500(\phi_5+\phi_6)$ $\Psi_3=0.577(\phi_1-\phi_4)+$ $+0.289(\phi_2-\phi_3-\phi_5+\phi_6)$	-	-	13
Naphthalene	$E_5=\alpha+0.618\beta$	$\Psi_5=0.425(\phi_1-\phi_4+\phi_5-\phi_8)+$ $+0.263(\phi_2-\phi_3+\phi_6-\phi_7)$	-	-	13
Anthracene	$E_7=\alpha+0.414\beta$	$\Psi_7=0.311(\phi_1-\phi_4-\phi_5+\phi_8)+$ $+0.220(\phi_2-\phi_3-\phi_6+\phi_7)+$ $+0.440(\phi_{10}-\phi_9)+$ $+0.091(\phi_{11}-\phi_{12}-\phi_{13}+\phi_{14})$	-	-	13
Cl-	$E_{Cl}=\alpha+2\beta$	$\Psi_{Cl}=\phi_{Cl}$	0.5	0.4	13
CH_3O-	$E_{CH_3O}=\alpha+2\beta$	$\Psi_{CH_3O}=\phi_O$	0.4*	1.0	14
C_2H_5O-	$E_{C_2H_5O}=\alpha+2\beta$	$\Psi_{C_2H_5O}=\phi_O$	0.4*	1.0	14
CH_3-	$E_1=\alpha+2.760\beta$ $E_2=\alpha-3.260\beta$	$\Psi_1=0.736\phi_C+0.677\phi_{H_3}$ $\Psi_2=0.677\phi_C-0.736\phi_{H_3}$	-0.5	0.8	13

*This work

symmetry than the unperturbed system and this may lift the degeneracy and may even mix the degenerate orbitals when the symmetry is sufficiently low. In the case of compounds 5 and 6 (symmetry D_{6h} and D_{3h}), the perturbation has no differentiating effect on orbitals Ψ_2 and Ψ_3.

Further decrease of symmetry lifts the two-fold degeneracy in compounds 7, 8 and 27 (symmetry: C_S, D_{2h} and C_{2v} respectively). Mixing of Ψ_2 and Ψ_3 occurs for compound 7 due to very low symmetry. Table 1 shows that I_D decreases with increasing destabilization of Ψ_{HO} in complete agreement with theory.

This is valid for both first and first- and second order perturbations. However this latter predicts a stabilization of Ψ_{HO} for compounds 23 and 25 leading to a higher I_D value than for the unsubstituted molecule. This is not born out by experiment.

The relationship between I_D and δE_{HO} has the general form

$$I_D = P + Q\delta E_{HO} \tag{11}$$

and it is illustrated by Fig. 2. It can be seen that the new ionization potential values of methyl-substituted naphthalenes decrease regularly with increasing first order destabilization of naphthalene Ψ_{HO} ($\delta E_5^{(1)}$) following the equation

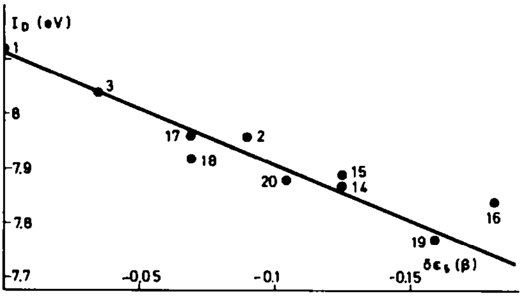

Fig. 2. Dependence of ionization potential on electronic structure for methyl-substituted naphthalenes.

$$I_D(ev) = 8{\cdot}11(\pm0{\cdot}02) + 2{\cdot}00(\pm0{\cdot}21)\delta E_5^{(1)}. \tag{12}$$

This changes to equation

$$I_D(ev) = 8{\cdot}11(\pm0{\cdot}03) + 1{\cdot}77(\pm0{\cdot}25)\delta E_5^{(1+2)} \tag{13}$$

Table 3. Correlations between ionization potentials and perturbations of the highest occupied molecular orbitals of various electron donor molecules

Compounds	Order	Slope Q	Intercept P	Correlation Coefficient r	Standard deviation σ
Methyl-substituted benzenes	1	2.49±0.31	9.12±0.12	0.977	0.13
	1+2	2.43±0.36	9.17±0.14	0.969	0.15
Methyl-sustituted naphthalenes*	1	2.00±0.21	8.11±0.02	0.965	0.03
	1+2	1.77±0.25	8.11±0.03	0.938	0.04
Methoxy-sustituted naphthalenes**	1	4.44±2.00	8.01±0.12	0.788	0.15
	1+2	3.07±1.15	8.00±0.09	0.883	0.13
Methyl-substituted anthracenes	1	0.35±0.49	7.40±0.03	0.579	0.03
	1+2	0.31±0.43	7.40±0.03	0.580	0.03

*Correlations established without compound No. 16 since σ (No. 16) > 3σ.

**The correlation for order 1 + 2 is calculated without compound No. 23 because of theoretical inconsistency.

when the total perturbation is considered.

The correlation is excellent, account being taken of the approximations involved in perturbation theory.

The results for the other homologous series are summarized in Table 3. The intercepts P are simply the I_D values of unsubstituted molecules. The agreement with the data reported in Table 1 is excellent. The slopes Q represent an "effective" value of the resonance integral β. In the case of methyl-substituted benzenes we have $\beta = 2{\cdot}4\text{–}2{\cdot}5$ eV which lies very close to the "spectroscopic" value of β: 2·3–2·6 eV.[15]

The results for the corresponding naphthalene derivatives can also be considered as satisfactory. However, the presence of methoxy groups almost doubles the β value, which drops to about 0·3 eV in the case of Me-substituted anthracenes. This casts doubt on the transferability of β values from one series to another.

In fact, when only one type of substituent is considered (here CH_3–), the effect of perturbation diminishes with increasing size of the unperturbed electronic system. The sensitivity to perturbation (slope Q) decreases in the order benzene > naphthalene > anthracene, causing a substantial variation of effective β values.

Let us note that for methoxy-naphthalenes and methyl-anthracenes the correlation is not very good due to very limited number of compounds studied. However this doesn't affect the general conclusions.

EXPERIMENTAL

The CT spectra have been recorded by a UNICAM SP800 spectrophotometer. The temp. was held constant within ±0·1°. The wave-length scale was controlled by the spectrum of Holmium. The reading uncertainty on $\bar{\nu}_{max}$ is about ±0·08 kK (~0·01 eV). The preparation and purification of materials have been described elsewhere.[12,16]

REFERENCES

[1] G. Briegleb, *Elektronen-Donator-Acceptor-Komplexe*; Springer Verlag, Berlin (1961).

[2] H. M. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.* **21**, 66 (1953).

[3] S. H. Hastings, J. L. Franklin, J. C. Schiller and F. A. Matsen, *J. Am. Chem. Soc.* **75**, 2900 (1953).

[4] G. Briegleb and J. Czekalla, *Z. Elektrochem.* **63**, 6 (1959).

[5] G. Briegleb, *Angew. Chem.* International Edition, 3, 617 (1964).

[6] R. Foster, *Nature* **183**, 1253 (1959).

[7] R. Foster, *Organic Charge-Transfer Complexes.* Academic Press, London (1969).

[8] R. S. Mulliken and W. B. Person, *Molecular Complexes*, A lecture and reprint volume, Wiley-Interscience, New York (1969).

[9] M. A. Slifkin and A. C. Allison, *Nature* **215**, 949 (1967).

[10] J. B.Nagy, O. B.Nagy and A. Bruylants, *J. Phys. Chem.* **78**, 980 (1974).

[11] V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev and Ye. L. Frankevich, *Bond Energies, Ionization Potentials and Electron Affinities.* Edward Arnold, London (1966).

[12] J. B.Nagy, O. B.Nagy and A. Bruylants, *Bull. Soc. Chim. Belg.* **82**, 337 (1973).

[13] E. Heilbronner and H. Bock, *Das HMO-MODELL und seine Anwendung.* Vol. I, II and III. Verlag Chemie, Weinheim Bergstrasse (1968).

[14] A. K. Colter and S. H. Hui, *J. Org. Chem.* **33**, 1935 (1968).

[15] J. R. Platt, *J. Chem. Phys.* **15**, 419 (1947).

[16] S. Dupire, J. B.Nagy, O. B.Nagy and A. Bruylants, *J. Chem. Soc. Perkin II*, 478 (1974).