Characterization of Intramolecular Charge-transfer Transitions. 1-Aryl-1,2,2-tricyanoethylenes and 7-Aryl-7,8,8-tricyanoquinodimethanes

Jun-ichi Aihara,* Kotaro Araya, and Yoshio Matsunaga

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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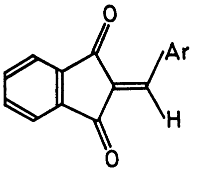
Synopsis. For the title compounds, the energy of the first electronic transition is linearly related to the vertical ionization potential of the aromatic nucleus (*e.g.*, benzene in the case of 1-phenyl-1,2,2-tricyanoethylene). This relationship gives a definite experimental support to the charge-transfer character of the electronic transitions concerned.

An intramolecular charge-transfer (CT) compound is an organic compound in which an electron-attracting group is attached to an electron-donor molecule, forming a single conjugated system as one whole.[1] In previous papers,[2-5] we have identified various types of compounds as such species by analyzing electronic spectra of the solutions and the condensed phases carefully. We found that, for a series of 2-(arylmethylene)-1,3-indandiones (A), the first intramclecular CT transition energy, $h\nu_{\mathrm{ICT}}$, can be expressed in the form:[4]

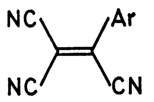
$$h\nu_{\mathrm{ICT}} = aI_{\mathrm{p}} - b, \qquad (1)$$

where a and b are constants which are substantially characteristic of the acceptor part (*i.e.*, 2-methylene-1,3-indandione), and where I_{p} is the vertical ionization potential of the donor part (*e.g.*, anthracene in the case of 2-(9-anthrylmethylene)-1,3-indandione). The same relationship was found to hold for the first absorption bands of 1-aryl-2,2-dicyanoethylenes (B).[5]

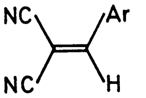
In this connection, we can fully anticipate the existence of such a linear relationship for the first absorption bands of 1-aryl-1,2,2-tricyanoethylenes (C) and for those of 7-aryl-7,8,8-tricyanoquinodimethanes (D) alike, because both tricyanoethylene and 7,8,8-tricyanoquinodimethane are supposedly good electron acceptors. If so, it would constitute the most conclusive evidence for a CT character of the electronic transitions concerned.[6]



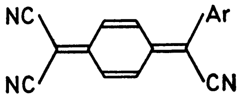
A



C



B



D

In order to see this, the spectroscopic data available on 1-aryl-1,2,2-tricyanoethylenes were first collected in Table 1.[7-13] The first absorption maxima of the seven 1-aryl-1,2,2-tricyanoethylenes in chloroform were then found to correlate well with the ionization potentials of the donor parts. As has been anticipated, a linear relationship between the two quantities was deduced therefrom with a correlation coefficient of 0.989. By the least-squares analysis, we obtain

$$(h\nu_{\mathrm{ICT}}/\mathrm{eV}) = 0.614\,(I_{\mathrm{p}}/\mathrm{eV}) - 2.14. \qquad (2)$$

It is now quite natural to attribute the first absorption band of every compound in Table 1 to the intramolecular CT transition from the highest occupied molecular orbital (HOMO), localized largely in the aryl group, to the lowest unoccupied molecular orbital (LUMO), localized largely in the tricyanoethylene part.

Next, Bespalov *et al.* prepared many 7-aryl-7,8,8-tricyanoquinodimethanes, and measured their electronic absorption spectra in acetonitrile.[14] They suggested that the first electronic transition might be of the CT type. This is exactly true from the present viewpoint. By the least-squares analysis, we again see with certainty the existence of a linear relationship between the first absorption maxima of these compounds[15] and the best vertical ionization potentials of the donor parts, namely,

$$(h\nu_{\mathrm{ICT}}/\mathrm{eV}) = 0.619\,(I_{\mathrm{p}}/\mathrm{eV}) - 2.78. \qquad (3)$$

The correlation coefficient is 0.969. We can, hence, attribute the first absorption band of every such compound to the intramolecular CT transition from the HOMO, localized largely in the aryl group, to the LUMO, localized largely in the tricyanoquinodimethane part.

Table 1. Intramolecular CT absorption bands of 1-aryl-1,2,2-tricyanoethylenes (C) in chloroform

Ar	$\dfrac{h\nu_{\mathrm{ICT}}}{10^3\ \mathrm{cm}^{-1}}$	$\dfrac{\varepsilon^{\mathrm{a)}}/\mathrm{mol}^{-1}}{\mathrm{dm}^3\,\mathrm{cm}^{-1}}$	$I_{\mathrm{p}}/\mathrm{eV}$
Phenyl	$29.15^{\mathrm{b)}}$	$16600^{\mathrm{b)}}$	$9.24^{\mathrm{f)}}$
2-Furyl	$26.11^{\mathrm{b)}}$	$25200^{\mathrm{b)}}$	$8.89^{\mathrm{g)}}$
p-Methoxyphenyl	$24.57^{\mathrm{b)}}$	$25400^{\mathrm{b)}}$	$8.54^{\mathrm{f)}}$
2-Pyrrolyl	$23.74^{\mathrm{c)}}$	$24300^{\mathrm{c)}}$	$8.20^{\mathrm{h)}}$
3-Indolyl	$21.86^{\mathrm{c)}}$	$20700^{\mathrm{b),e)}}$	$7.79^{\mathrm{i)}}$
p-Dimethylaminophenyl	$19.46^{\mathrm{c)}}$	$53100^{\mathrm{c)}}$	$7.51^{\mathrm{f)}}$
3-Indolizinyl	$18.76^{\mathrm{d)}}$	$33200^{\mathrm{d)}}$	$7.24^{\mathrm{j)}}$

a) Molar absorptivity. b) Ref. 7. c) Present work. d) Ref. 8. e) Value measured in acetone solvent. f) Ref. 9. g) Ref. 10. h) Ref. 11. i) Ref. 12. j) Ref. 13.

Here, it is noteworthy that, as in the case of 2-(arylmethylene)-1,3-indandiones[4] and 1-aryl-2,2-dicyanoethylenes,[5] the a value is relatively small for both 1-aryl-1,2,2-tricyanoethylenes and 7-aryl-7,8,8-tricyanoquinodimethanes. Considering that the a value for binary CT complexes usually lies in the 0.82—0.97 range,[16] the a=0.614 value for 1-aryl-1,2,2-tricyano-

Table 2. The relationship $h\nu_{ICT}=aI_p$-b for intramolecular CT transitions

Type of compounds	Solvent	a	b/eV
A$^{a)}$	Chloroform	0.592	1.84
B$^{b)}$	Chloroform	0.675	2.23
C$^{c)}$	Chloroform	0.614	2.14
D$^{c)}$	Acetonitrile	0.619	2.78

a) Ref. 4. b) Ref. 5. c) Present work.

ethylenes and the a=0.619 value for 7-aryl-7,8,8-tricyanoquinodimethanes are obviously small. The a values determined for the four types of intramolecular CT bands are summarized in Table 2. It has now been established that the a value is close to 0.6 in the case of typical intramolecular CT bands measured in solution. According to Flurry's molecular orbital description of CT transitions,$^{17)}$ the $a\approx0.6$ value indicates that about 1.6 of the two frontier electrons, on the average, reside in the donor ring in the ground state. Therefore, all these intramolecular CT compounds can assuredly be regarded as undissociable CT complexes.

On the other hand, the b value reflects the acceptor electron affinity and some other effects including structural factors, so it is quite difficult to analyze the b value in detail. However, the smallest b value for 2-(arylmethylene)-1,3-indandiones may be an indication of the smallest electron affinity of the common acceptor part (*i.e.*, 2-methylene-1,3-indandione).

In 1953, the study of intramolecular CT spectra was initiated with monosubstituted benzenes, such as aniline and benzaldehyde.$^{1)}$ We have now a number of colorful intramolecular CT compounds, which are quite similar in many respects to binary CT complexes.$^{4)}$ Most of them indeed show CT absorption bands isolated in the visible region. These compounds can, hence, be viewed as model compounds of binary CT complexes, each with a fairly fixed molecular geometry. As suggested in previous papers,$^{4,5)}$ they will be of great help in obtaining insight into various electronic processes related to the CT transition in binary CT complexes.

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15) In order to obtain Eq. 3, we used the absorption maxima of the compounds where aryl groups are phenyl, *p*-chlorophenyl, *p*-tolyl, *p*-hydroxyphenyl, *p*-methoxyphenyl, *p*-aminophenyl, 3-indolyl, *p*-dimethylaminophenyl, and 1-azulenyl.$^{14)}$

16) See *e.g.* G. Briegreb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin (1961); R. Foster, "Organic Charge-Transfer Complexes," Academic Press, London (1969).

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