Tetrahedron, 1966, Vol. 22, pp. 101 to 110. Pergamon Press Ltd. Printed in Northern Ireland

CHARGE-TRANSFER ACCEPTORS

INDANETRIONE

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(*Received* 21 *April* 1965; *in revised form* 7 *July* 1965)

Abstract—A hypothesis for the design of organic charge-transfer acceptors is proposed and tested. The acceptor structure criteria include: (1) electron withdrawing power of substituents, (2) the number and location of substituents, and (3) the conjugated system to which groups are attached. This hypothesis, applied to modification of the substituents in phthalic anhydride, leads to the prediction that indanetrione should be an effective acceptor with an electron affinity between 0·7 and 1·2 eV. Indanetrione was prepared by thermal dehydration of ninhydrin. π-Complexes of indanetrione were measured and compared with the charge-transfer absorption of tetracyanoethylene and the same donors. The electron affinity of indanetrione, 1·1 eV, determined in this fashion, was in excellent agreement with the predictions.

INTRODUCTION

THE theory of charge-transfer spectra, as originally postulated by Mulliken[2] using a valence bond treatment, has been widely applied. Simplifying assumptions on this theory include linear relationships,[3] inclusion of overlap terms[4], and variation procedures.[5]

The most commonly employed method,[3] as reviewed,[4,6,7] gives the energy of the charge-transfer transition, E_π, in terms of the donor ionization potential IP and the acceptor electron affinity EA, Eq. 1,

$$E_\pi = IP - EA + C \qquad (1)$$

where the constant, C, is a collective term for solvation, polarization and non-bonding contributions. By using a single acceptor and a set of donors with known ionization potentials, values of EA + C for individual acceptors have been obtained.

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[2] R. S. Mulliken, *J. Amer. Chem. Soc.* **72**, 600 (1950); **74**, 811 (1952).

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

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

[5] H. Yada, J. Tanaka and S. Nagakura, *Bull. Chem. Soc., Japan* **33**, 1660 (1960).

[6] R. S. Mulliken and W. G. Person, *Ann. Rev. Phys. Chem.* **13**, 107 (1962).

[7] L. J. Andrews and R. M. Keefer, *Molecular Complexes in Organic Chemistry.* Holden-Day, San Francisco (1964).

The same limited acceptor concept has been applied to charge-transfer solvent shifts,[7,8] transition polarization[9] and multiple transitions.[10,11]

Recently, however, a molecular orbital treatment has been applied to complexes.[12] Studies were mainly restricted to single acceptors and sets of donors for which direct calculations could be made. Since the ionization potentials are not known for many of the high mol. wt. donors, Eq. 2 was used for acceptor evaluation,[12–14] perturbation

$$E_\pi = B_j - (\alpha + x_i\beta) \tag{2}$$

calculation of donor substituents,[15] and multiple charge-transfer transitions.[16] In Eq. 2, B_j is the energy of the acceptor orbital receiving the transferred electron, α is the coulomb or localized charge integral, β is the resonance or charge interaction integral, and x_i is the energy level coefficient for the highest occupied orbital in the complex.

Although the molecular orbital method shifts the emphasis from empirical data to theoretical calculations for the donor molecule, no similar analysis of acceptors in the charge-transfer complex has been developed. The few attempts toward a broad understanding of acceptor characteristics[17,18] have been restricted to evaluation of the electron affinity, EA.

In this study, we have therefore attempted to set up a qualitative acceptor hypothesis and to test this hypothesis by predicting and determining the charge-transfer properties of a new acceptor.

The acceptor hypothesis. Since all compounds have some electron affinity, the hypothesis seeks to establish requirements for improving acceptor characteristics. This is done by setting up criteria for the relationship of structure to electron affinity. Because of their direct application to this study, materials considered in this section are limited to organic compounds which are known to or might be predicted to act as charge-transfer acceptors.

The qualitative criteria of the acceptor hypotheses were derived from a comparison of structures and electron affinities of many acceptors. However, a select sample from the literature,[18] Table 1, provides the basis for understanding these criteria. Fundamentally it can be seen that the criteria must allow for substituents and the ability of these substituents to effect one another.

Perhaps the most obvious characteristic in these compounds is that of the substituents themselves. All the acceptors in Table 1 have nitrile or cyclic anhydride substitution.

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[8] N. B. Jurinski and P. A. D. deMaine, *J. Amer. Chem. Soc.* **86**, 3217 (1964); C. Reichardt, *Angew. Chem. internat. Ed.* **4**, 29 (1965).

[9] M. Chowdhury and L. Goodman, *J. Amer. Chem. Soc.* **86**, 2777 (1964).

[10] E. M. Voigt, *J. Amer. Chem. Soc.*, **86**, 3611 (1964); E. M. Voigt and C. Reid, *Ibid.* **86**, 3930 (1964); A. Zweig, *Tetrahedron Letters* **89** (1964).

[11] G. Breigleb, J. Czekalla and G. Reuss, *Z. Phys. Chem.*, *N. F.* **30**, 316 (1961).

[12] M. J. S. Dewar and A. R. Lepley, *J. Amer. Chem. Soc.* **83**, 4560 (1961).

[13] M. J. S. Dewar and H. Rogers, *J. Amer. Chem. Soc.* **84**, 395 (1962).

[14] A. R. Lepley. *J. Amer. Chem. Soc.* **84**, 3577 (1962).

[15] A. R. Lepley, *J. Amer. Chem. Soc.* **86**, 2545 (1964).

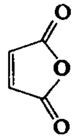
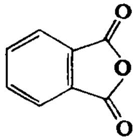
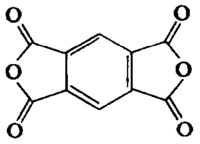
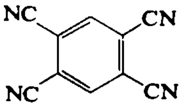
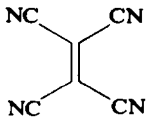
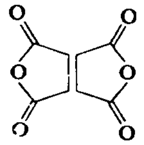
[16] A. R. Lepley, *Tetrahedron Letters* 2823 (1964).

[17] R. Foster, *Tetrahedron* **10**, 96 (1960); R. Foster and T. J. Thompson, *Trans. Faraday Soc.* **59**, 296 (1963).

[18] G. Briegleb, *Angew. Chem.* **76**, 326 (1964).

From the structurally similar pair, pyromellitic dianhydride and 1,2,4,5-tetracyanobenzene, we deduce that the cyclic anhydride group is more effective than cyano groups in promoting electron affinity. A more quantitative evaluation of this effect has recently been shown for mono-substituted *p*-benzoquinones.[19] The electron affinity for a series of acceptors was shown to be directly proportional to the Hammett σ_p for the substituent. Our broader if less exact comparison indicates that substituents[20] with $\sigma_p > 0{\cdot}60$ (i.e., $CN = 0{\cdot}66$, $NO_2 = 0{\cdot}78$) are particularly effective in charge-transfer acceptors. In terms of general resonance theory, this criterion might be simply expressed by the electron withdrawing power of the substituent The greater the electron withdrawing power of the substituents the better the acceptor.

TABLE 1. ELECTRON AFFINITIES OF RELATED ACCEPTORS AS DETERMINED FROM THEIR MOLECULAR COMPLEX CHARGE-TRANSFER SPECTRA[a]

Name	Structure	EA (ev)
Maleic anhydride		$0{\cdot}4_2$
Phthalic anhydride		$0{\cdot}1_5$
Pyromellitic dianhydride		0·85
1,2,4,5-Tetracyanobenzene		0·4
Tetracyanoethylene		1·80
Ethylenetetracarboxylic dianhydride		unknown

[a] Ref. 18.

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[19] P. R. Hammond, *J. Chem. Soc.* 471 (1964).

[20] cf. tabulations of: C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.* 2, 323 (1964).

This criterion does not indicate how several substituents on a structure influence its electron affinity. The set of compounds phthalic anhydride and pyromellitic dianhydride exemplify these variables. The electron affinity increases with the number of substituents, but not in a direct proportionality. The σ_p must be separated into resonance and inductive components before effects of multiple substituents can be correlated through molecular orbital perturbation calculations.[21] Perturbation calculations of substituent parameters for the donor molecule in π-complexes have been demonstrated.[15] Although the relative perturbation values involve the atomic orbital coefficients at the position of substitution, the electron affinity of an acceptor generally increases with the number of strong electron withdrawing substituents, the amount of this increase being dependent on the location of these substituents in the acceptor structure.

A third criterion is apparent from the comparison of maleic anhydride to phthalic anhydride or tetracyanoethylene to 1,2,4,5-tetracyanobenzene. The electron affinities of the aromatic compounds are appreciably smaller than those of the ethylenic compounds. This effect is a general phenomena in conjugated systems and depends on the delocalization energy. The effect on the lowest non-bonding level is calculated directly by molecular orbital methods. In the simple form used in the approximations for equation 2, the constant values of α and β aid in structural correlations. The value of B_j is equal to α-$x_j\beta$ as calculated for the parent hydrocarbon with substituent perturbation corrections. Therefore the lowest unoccupied orbital coefficient, x_j, is characteristic of the acceptor, Eq. 3.

$$E_\pi = -\beta(x_j + x_i) \tag{3}$$

β itself is negative so that a decrease in x_j decreases the electron affinity in the acceptor. Since x_j decreases with an increase in the extent of a conjugated system,[22] the acceptor electron affinity decreases with increasing conjugation.

An additional factor which effects the ability of a compound to act as a π-complex acceptor but does not influence its electron affinity is molecular planarity. All of the compounds in Table 1 are planar, but tetranitromethane and other non-planar molecules also act as acceptors. The application of molecular orbital theory in its simplest form to a whole complex model has been accomplished using aromatic donors.[12–16] Out-of-plane structural features, particularly near the site of the electron withdrawing groups, may prevent the close association of donor and acceptor needed for π-complex formation. Although this last feature is not a necessary component in the general acceptor hypothesis, it applies in this particular study.

In summary, *the electron affinity in a conjugated organic charge-transfer acceptor increases with:*

1. The electron withdrawing power of substituents,
2. The number of substituents depending on location,
3. Restricted size of the conjugated system.

A better understanding of the implications of the criteria is obtained by consideration of an example. In the sections which follow, the hypothesis is applied to

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[21] M. J. S. Dewar and P. J. Grisdale, *J. Amer. Chem. Soc.* **84**, 3539, 3541, 3546, 3548 (1962).

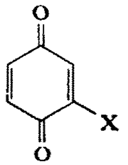
[22] cf. C. A. Coulson and R. Daudel, *Dictionary of Values of Molecular Constants.* Mathematical Institute, Oxford, England, and the Centre de Chimie Theorique de France, Paris, France (1955).

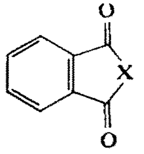
predict (a) an acceptor structure and (b) a rough value for the electron affinity of this acceptor. Chemical data on the preparation of this acceptor and its spectroscopic evaluation complete the example.

Acceptor prediction. The suggestion of ethylenetetracarboxylic dianhydride as a potent charge-transfer acceptor is a direct extension of the data in Table 1. However, this projection, using only criterion 2, requires both substituent group parameters and perturbation calculations for estimation of the electron affinity. A simpler if not totally determinant projection involves the modification of a substituent. Phthalic anhydride was chosen for this purpose.

The anhydride group can be modified by the replacement of the oxygen link with other bridging atoms or groups such as —S—, —SO—, —NH—, or —CO—. Although σ_p values are not available for these groups, the comparable set[20] for fully methylated compounds is $—OCH_3 = -0{\cdot}27$, $—SCH_3 = 0{\cdot}00$, $—SOCH_3 = 0{\cdot}49$, $—N(CH_3)_2 = -0{\cdot}83$, and $—COCH_3 = 0{\cdot}50$. If a shift parallel to that in the *p*-benzoquinones,[19] Eq. 4, was applied to the replacement of oxygen in phthalic anhydride, these

$$E_\pi = 0{\cdot}7\sigma_p + 2{\cdot}9 \tag{4}$$





σ_p values might be used to predict EA. Eq. 1 has been simplified[6,18] to determine electron affinities by the comparison of acceptors (primed and unprimed sets), Eq. 5, where a common donor, IP, is used and the complexes have similar interactions,

$$EA + E_\pi = EA' + E_\pi' \tag{5}$$

i.e., C = C′. Substitution of E_π values in Eq. 5 by those in Eq. 4 gives Eq. 6.

$$EA - 0{\cdot}7\sigma_p = EA' - 0{\cdot}7\sigma_p' \tag{6}$$

Since EA for phthalic anhydride was 0·15 ev, an increase in EA′ for the modified compound occurs when σ_p' (methylated) is greater than the $-0{\cdot}27$ of methoxy. The order of increasing acceptor strength should therefore parallel the increase in σ_p: $—N(CH_3)_2 < —OCH_3 < —SCH_3 < —SOCH_3 \cong COCH_3$.

At least one additional correction should be imposed on Eq. 6. The original formulation allowed for only a single substituent while our system modifies two substituents (or locations) in the conjugate structure. If we consider our change a modification of the anhydride group and assume an additive effect due to modification, no direct perturbation calculation need be made. The anhydride bridge is then effectively two adjacent substituents on benzene and the effect of the bridge group is distributed between both groups. Eq. 6a corrects for this error through assignment of some value n for the composite group.

$$EA - n0{\cdot}7\sigma_p = EA' - n0{\cdot}7\sigma_p' \tag{6a}$$

Since methylated σ_p values are being used, the value for n should be between 1 and 2. Calculating a value for carbonyl substitution, indanetrione should have an electron affinity between 0·7 ev if $n = 1$, and 1·2 ev if $n = 2$. This structure, X = —CO—, should be the most effective of those considered,[23] and has been studied as a test of the hypothesis.

Preparation of indanetrione and related compounds. The compound predicted by the qualitative acceptor structure hypotheses, indanetrione (I), was prepared by thermal dehydration of ninhydrin (II), and purified by simultaneous sublimation. When dehydration of ninhydrin was attempted by continuous extraction with methylene chloride, both the red trione and a yellow solid precipitated from the deep green solution. The yellow compound was readily separated because of its low solubility in this solvent.

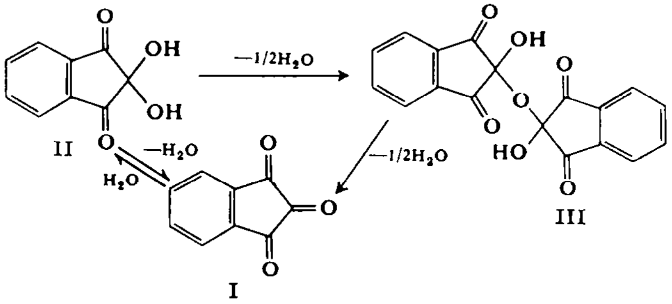


Diagram A

The new yellow compound could be converted thermally into indanetrione but showed a higher conversion temperature, 153–155°, as compared with ninhydrin, 136–139°. At the dehydration point, sometimes referred to as the m.p.[24,25] the solids become a ruby red. Melting does not occur until 255° when an emerald liquid forms. This liquid decomposes to an intractable brick red solid when held at temperatures above 255°.

Since ninhydrin is reportedly autoxidizable to phthalic anhydride,[24] we compared the IR spectra of the yellow material, ninhydrin, indanetrione and phthalic anhydride. Each spectrum contained some bands which did not overlap the peaks of the other compounds. Ninhydrin has only one such distinct band at 1005 w cm^{-1}, which could be lost under a strong nearby band of phthalic anhydride. Phthalic anhydride shows distinct peaks at 1110 m, 910 s, and 715 s, while indanetrione has such peaks at 984 w, 839 w, and 754 m cm^{-1}. By contrast, the yellow compound has distinct peaks at 1200 m, 1055 m, 1030 w, 965 m, 778 w, 770 w, 762 w, and 693 w cm^{-1}. The 1250 — 950 cm^{-1} region of the yellow compound's characteristic infrared absorption bands corresponds to that of the carbon-oxygen single bond stretching vibration of ethers and esters.[26]

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[23] A list of several additional effective acceptors predicted by this hypothesis will be furnished by the authors on request.

[24] A. Schonberg and R. Moubacher, *J. Chem. Soc.* 71 (1943).

[25] D. J. McCaldin, *Chem. Revs.* **60**, 39 (1960).

[26] R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds* p. 60. J. Wiley New York (1963).

Elemental analysis on the yellow material indicated that the carbon and hydrogen content was between that of ninhydrin and indanetrione. Since these compounds were interconverted by the loss or addition of water, we postulated a dimeric hemiketal (III) for the yellow material, Diagram A. This structure satisfies both the infrared characteristics and elemental analysis.

Visible spectra and charge-transfer characteristics. The red crystalline indanetrione has a maximum solubility of 0·54 g/100 ml at 25° giving a bluish-green solution, Fig. 1, with an absorption maximum at 609 mμ, ϵ_{Max} 21·9 ± 0·4. Solutions of the trione may be prepared rapidly with the powered red crystals and by prolonged standing or several hours reflux with ninhydrin. The solution is quite sensitive to moisture but may be stored over pelletized Linde 5A Molecular Sieve. Although solutions of indanetrione with a bluish-green color were reported in hot benzene, nitrobenzene and glacial acetic acid,[24] absorption spectra were not reported. The spectroscopic measurements of MacFadyen[27] did not give wavelength values above 400 mμ or molar absorptivities, $\epsilon_{\text{max,}}$ below 500. However, he proposed that the formation of indanetrione gave rise to the red color of concentrated sulfuric acid solutions of ninhydrin.

The blue-green methylene chloride solution of indanetrione gave color changes when aromatic hydrocarbons were added. The spectra of these mixtures retain the sharp peak at 609 mμ, but in addition show characteristic increases in the absorption between 380 and 600 mμ. Although the new charge-transfer bands were broad, most showed a characteristic maximum or shoulder which was used in wavelength assignments, Table 2. None of the donor hydrocarbons used absorbs in the region of its charge-transfer maximum. However, corrections for the acceptor indanetrione were made. Literature data[11,13,28,29] for tetracyanoethylene complexes with the same donors was supplemented with measurements for acenaphthene and 3,4,5,6-dibenzophenanthrene. Fig. 2 plots the values of E_π for the two acceptors. The observed linear relationship and slope of unity agree with the limitation of $C = C'$ on Eq. 5. The deviation of the hexamethylbenzene value may result from a failure to meet this restriction. Initial analysis of the hexamethylbenzene data at 10 and 40° indicate a change from a 2:1 to a 1:1 complex.

Calculations of the electron affinity of indanetrione were made using Eq. 5. Both charge-transfer and the best mean value from all sources for the tetracyanoethylene electron affinity[18] were used in obtaining the values of Table 3. The charge-transfer value, 1·07 ev, for indanetrione compares well with the previous predictions and gives a value of $n = 1\frac{2}{3}$ for Eq. 6a.

The lowest unoccupied orbital coefficient, x_j, for indanetrione can be obtained if constant donor x_i values are used in Eq. 3. Eq. 7 is the molecular orbital analog of Eq. 5.

$$x_j\beta + E_\pi = x_j'\beta + E_\pi' \tag{7}$$

Using $\beta = -3{\cdot}06$ ev from the charge-transfer measurements[13] for tetracyanoethylene, the value of x_j for indanetrione is 0·38, Table 3. This value of β has been shown to be valid for a wide range of acceptors.[12–14]

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[27] D. A. MacFadyen, *J. Biol. Chem.* **186**, 1 (1950).

[28] R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.* **80**, 2778 (1958).

[29] D. J. Cram and R. H. Bauer, *J. Amer. Chem. Soc.* **81**, 5971 (1959).

TABLE 2. THE LOWEST ENERGY CHARGE-TRANSFER ABSORPTION MAXIMA FOR HYDROCARBON COMPLEXES WITH INDANETRIONE OR TETRACYANOETHYLENE

Donor			Charge-transfer absorption maxima	
No.	Compound	Highest occupied orbital coefficient,[a] $x_1(\beta)$	Indanetrione $\lambda(m\mu)$	Tetracyanoethylene $\lambda(m\mu)$
1	Acenaphthene	0·51[b]	456 ± 5	653 ± 2
2	Anthracene	0·414	503 ± 5	740[c]
3	3,4-Benzpyrene	0·371	541 ± 5	820[d]
4	3,4,5,6-Dibenzo-phenanthrene	0·535	440 ± 5	645 ± 5
5	Hexamethylbenzene	0·64[b]	433 ± 5	545[e]
6	[2.2]-Paracyclophane	0·67[b]	395 ± 15	521[f]
7	Perylene	0·347	560 ± 5	920[d]
8	Phenanthrene	0·605	400 ± 10	540[d]
9	Pyrene	0·445	481 ± 5	724[e]
10	Triphenylene	0·684	405 ± 10	570[d]

[a] Ref. 22.

[b] estimated from the TCNE-complex wavelength correlation of Ref. 13.

[c] Ref. 11.

[d] Ref. 13.

[e] Ref. 28.

[f] Ref. 29.

The electron affinity of indanetrione exceeds that of even pyromellitic dianhydride, Table 1.

TABLE 3. ELECTRON AFFINITIES, EA, AND LOWEST UNOCCUPIED ORBITAL COEFFICIENTS, x_j, FOR TETRACYANOETHYLENE AND INDANETRIONE

Acceptor	EA_{ct}[a]	$\overline{EA}$[b]	$x_j\beta$	x_j[c]
Tetracyanoethylene	1·90[d]	1·80[d]	−·34	·11[e]
Indanetrione[f]	1·07	·97	−1·17	·38

[a] Electron affinity from charge-transfer, Ref. 18.

[b] Mean electron affinity from all sources, Ref. 18.

[b] From $\beta = -3{\cdot}06$ for tetracyanoethylene, Ref. 13.

[d] Ref. 18.

[e] Ref. 13.

[f] Average deviation, applicable to all values is ±·04.

Comparison with more extensive acceptor compilations[18] shows that this conjugated cyclic trione is equivalent to trinitrofluorenone or the dichoro-*p*-benzoquinones in electron affinity.

Although the hypotheses needs further quantitative refinement, the qualitative criteria discussed provide a means for predicting structures of interest as potential charge-transfer acceptors.

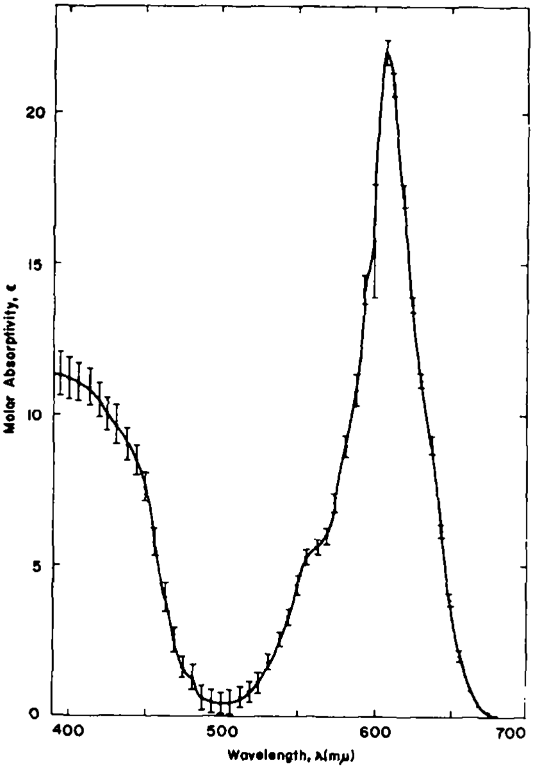

FIG. 1 Variation of the molar absorptivity, ε, with wave length, λ, for indanetrione in methylene chloride at 25·0 ± 0·1°. Root mean square deviations from the least squares calculations of ε are indicated.

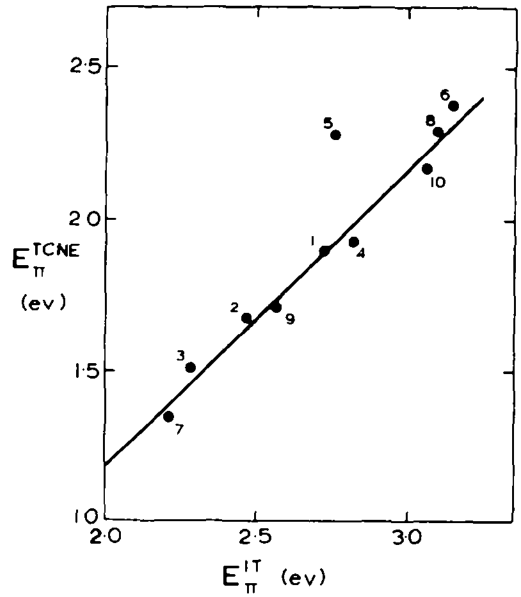

FIG. 2 A plot of the charge-transfer energies, E_π, for tetracyanoethylene (TCNE) and indanetrione (IT) π-complexes with several donor hydrocarbons. Point designation corresponds to the numbering of the donors in Table 2.

EXPERIMENTAL[30]

Indanetrione (I). Ninhydrin was thermally converted to indanetrione. Sublimation at 125° (bath) in a standard glass apparatus gave thin needle-like red crystals which rapidly picked up moisture from the air, reverting to ninhydrin. A more stable crystalline form collected on the door when heated in a vacuum oven, National Appliance Co., Model 5810, at 135–140° (oven) and 0·3–7·0 mm for 12 hr. Heavy deep red platelets of indanetrione, 7·6 g (83% yield) were obtained from 9·2 g of practical ninhydrin (Pierce). Physical properties of indanetrione were mp. 255–257° (lit.[24] 255°), IR peaks at 3200 m, 3100 m, 1770 s, 1750 s, 1725 vs*, 1595 m, 1415 w, 1375 w, 1355 w, 1300 w, 1240 m, 1230 m, 1185 s, 1160 m, 1080 m, 1070 m, 1020 w, 984 w, 945 m, 892 w, 839 w, 754 m, and 741 m cm^{-1}. (Found: C, 67·27; H, 2·73. Calc. for $C_9H_4O_3$: C, 67·50; H, 2·50%.)

Indanetrione produced in this fashion has been stored in plastic capped vial for 6 months without appreciable surface whitening due to moisture.

Dimeric hemiketal of ninhydrin (III). Continuous Soxelet extraction with CH_2Cl_2 for 24 hr dissolved 10·8 g ninhydrin and gave 2·76 g (27%) conversion to a yellow powder. The remaining material was dissolved in the deep green solution or deposited as a purple solid. The purple compound was removed by repeated washing with cold anhydrous CH_2Cl_2. The yellow solid was thermally converted into a red solid at 153–155°. The red solid had the same m.p. as indanetrione (255–257°). The yellow dimeric hemiketal had IR absorption bands at 3430 m, 3200 m, 3120 m, 1770 s, 1730 s*, 1600 m, 1470 vw, 1415 w, 1375 w, 1300 w, 1255 w, 1230 w, 1200 m, 1185 s, 1160 m, 1080 s, 1055 m, 1030 w, 1020 m, 965 m, 942 s, 925 w, 893 w, 815 vw, 798 vw, 778 w, 770 w, 762 w, 743 s, and 693 w cm^{-1}. (Found: C, 63·76; H, 2·97. Calc. for $C_{18}H_{10}O_7$: C, 63·91; H, 2·98%.)

The yellow hemiketal, 2·75 g, gave 0·5 g (18%) of indanetrione when heated in the oven under vacuum for 12 hr.

Ninhydrin (II). Ninhydrin of high purity can be quantitatively recovered from indanetrione by addition of the calculated amount of water. The thermal conversion point of this material was 136–139° (Lit.[24] 139°) at atm. press., and is normally referred to[25] as the m.p. of ninhydrin. The solid changes color, white to red, at this point but melts to an emerald liquid at 255° (m.p. of indanetrione). Ninhydrin has IR peaks at 3300 s, 1750 s, 1685 s*, 1585 m, 1380 m, 1290 w, 1250 w, 1185 s, 1155 m, 1080 m, 1065 m, 1015 w, 1005 w, 947 s, 890 w, and 744 s cm^{-1}.

IR spectrum of phthalic anhydride. A comparison spectrum of commercial phthalic anhydride gave IR peaks at 3080 m, 1855 m, 1770 s*, 1600 w, 1470 w, 1385 vw, 1360 w, 1335 w, 1265 s, 1212 w, 1175 w, 1110 m, 1075 w, 1010 w, 910 s, 843 w, 803 w, 741 vw, 715 s, and 677 w cm^{-1}.

Visible spectra. The materials were dissolved in anhydrous spectroscopic CH_2Cl_2.[31] Varying amounts of stock solutions of donor (0·02 to 0·2M) and indanetrione (0·01 to 0·02M), were mixed. The spectra of the solutions was measured at 25·0 ± 0·1° with a Beckman DK-2 Spectrophotometer. Holmium oxide glass was used for wavelength calibration in the region studied, 350–750 mμ. Extinction coefficients, ϵ, for indanetrione were calculated by computer using a least squares fit of Beer's law. Root mean square deviations are indicated for these values. Wavelength maxima for charge-transfer complexes were assigned by determination of the mid-point on the broad peak of the complex. Corrections were made for absorption of the acceptor in these assignments. Complex wavelength deviations were determined from corrections, curve shape and spectrophotometer calibrations. Wavelength values are given in mμ for λ or electron volts for E_{π}.

[30] Analyses were performed by Schwarzkopf Microanalytical Laboratory, 56–19 37th Ave., Woodside 77, New York. IR spectra were measured in KBr discs and analyzed as previously described, A. R. Lepley and R. H. Becker, *Tetrahedron* **21**, 2365 (1965). Materials other than those included have been described in Ref. 12-14.

[31] Because of the ease with which indanetrione reacts with moisture, amines, alcohols and ketones, the purity of the solvent must exceed that of normal spectro grade. Passage of CH_2Cl_2 through a 20 cm column of activated alumina removed reactive inpurities.