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The Electron Affinities of Organic Electron Acceptors

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The principal methods used to determine the electron affinities of organic molecules are examined and the published data in this field are analysed. Briegleb's series, used in the majority of instances, yields absolute values which are too low. The most probable absolute electron affinities are quoted for the majority of organic electron acceptors investigated and their dependence on substituents and structural features is analysed.
The bibliography includes 121 references.

CONTENTS

I.	Introduction	503
II.	Fundamental concepts	503
III.	Methods for the determination of electron affinity	504
IV.	Electron affinities of neutral electron acceptors	507

I. INTRODUCTION

The electron affinities of organic molecules and ions are nowadays essential for the interpretation of the results in a very wide variety of research fields, associated mainly with the study of the properties of charge-transfer complexes and their role in organic, catalytic, and biological processes [1-7] as well as the study of one-electron transfer reactions [6,8], organic semiconductors [9-11], and organic materials with metallic conduction [12,13]. The publication of the handbook of Gurvich et al. [14] made available a large number of experimental electron affinities of organic acceptors but did not in any way solve the problem of their utilisation, since the results obtained by various workers for the same acceptors frequently differ by more than 1 eV.

The aim of the present review is to select from the available experimental data the most reliable electron affinities of organic acceptors. We also hope that the review will draw the attention of new investigators to the problem of the determination of electron affinities, which will directly assist in its final solution.

Since this review deals with compounds having fairly distinct electron-accepting properties, aromatic hydrocarbons, heterocyclic compounds, and other compounds with a negative or small positive electron affinity are excluded.

Among the methods for the determination of electron affinities, quantum-mechanical calculations are not considered, since we believe that they should be the subject of a separate review.

II. FUNDAMENTAL CONCEPTS

Electron capture in the gas phase can be most conveniently treated in relation to a neutral diatomic molecule AB. This process can be regarded as a transition between two vibronic levels [15], one of which characterises the neutral molecule AB and the other the corresponding

radical-anion $AB^{\cdot-}$. Case *a* (Fig. 1) represents dissociative electron capture. Electrons whose kinetic energy varies from E_1 to E_2 are captured, while those having other kinetic energies are scattered. In case *b* (Fig. 1), the capture of electrons with a kinetic energy in the range $E_4 < E_{kin} < E_3$ leads to vibrational excitation of the radical-anion $AB^{\cdot-}$, which is stabilised in collisions with other species. The potential energy curve for the radical ion has a minimum. In case *c*, the molecule can capture an electron only in a vibrationally excited state and the radical-ion is stabilised in subsequent collisions between molecules.

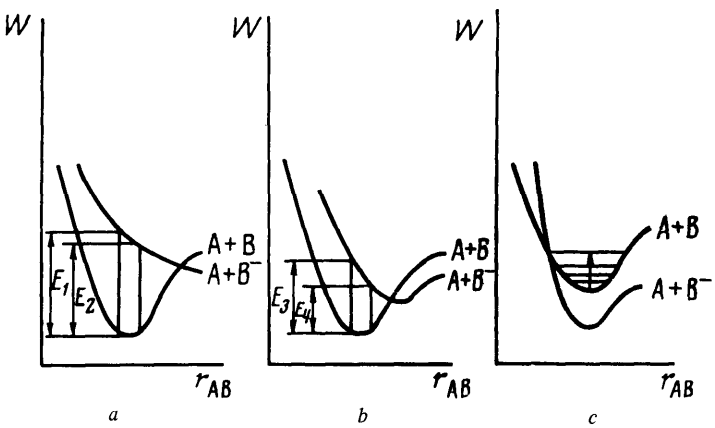


Figure 1. Electron capture by a diatomic molecule AB.

It is noteworthy that only in the last case does the molecule AB have a positive electron affinity (EA). Electron affinity is an energetic characteristic of electron capture processes and is equal to the amount of energy consumed or evolved when an electron is added to a gas-phase molecule in the state with minimum energy. Depending on whether the electron adds to a radical-ion in the ground (equilibrium) or vibrationally excited state, adiabatic (thermodynamic) and vertical electron affinities are distinguished. All the foregoing considerations may be expressed by the following equations:

$$AB + e \rightleftarrows AB^{\cdot-},$$
$$EA\ (\text{adiabatic}) = E(AB^{\cdot-}, r_{AB^{\cdot-}}) - E[(AB, r_{AB}) + e],$$
$$EA\ (\text{vertical}) = E(AB^{\cdot-}, r_{AB}) - E[(AB, r_{AB}) + e],$$

where E is the total energy of the $AB^{\cdot-}$ and AB species in the equilibrium ($AB^{\cdot-}$, $r_{AB^{\cdot-}}$ and AB, r_{AB}) and vibrationally excited (AB^{-}, $r_{AB^{-}}$) states.

By definition, the adiabatic ionisation potential (IP) of the radical-anion $AB^{\cdot-}$ is expressed as follows:

$$-IP_{ad}(AB^{\cdot-}) = E[(AB, r_{AB}) + e] - E(AB^{\cdot-}, r_{AB^{\cdot-}})$$

and

$$EA_{ad}(AB) = IP_{ad}(AB^{\cdot-}).$$

The above relation is invalid for vertical processes.

Examination of processes of this kind for polyatomic molecules does not entail fundamental difficulties, although it is much more complex owing to the larger number of degrees of freedom. In principle, a molecule can combine not only with the first electron to form a radical-anion, but also with a second electron to form a dianion. In the latter case, one is dealing with the second electron affinity. In the gas phase, such processes are extremely improbable, but they are known in the condensed phase, where their occurrence is promoted by the strong solvation of charged species.

Electron affinities in the gas and condensed phases are also distinguished. In the condensed phase, the electron affinity does not characterise an individual molecule but a molecule in a crystal lattice or a solvation shell and is correspondingly increased by the polarisation (P) or solvation[9] (E_{solv}) energy:

$$EA_{cr} = EA + P$$
$$EA_{solv} = EA + EA^{\cdot-}_{solv} - E^{A}_{solv}.$$

III. METHODS FOR THE DETERMINATION OF ELECTRON AFFINITY

The fundamental methods for the determination of electron affinity have been examined in a number of monographs and reviews[15-23]. Most of them are indirect, permitting the calculation of electron affinity from the general energetics of the given process. Some of them are related to the study of the given electron-accepting molecule in a condensed medium.

Photochemical Elimination of Electrons from Negative Ions (The Photoabstraction Method)

This is a direct and most accurate method for the determination of electron affinities[20,21,24,25]. After their generation, capture, and detection, negative ions are irradiated with monochromatic light having a smoothly varying frequency. When the threshold photon energy is reached, the photoabstraction of electrons from the negative ions $A^{\cdot-}$ begins:

$$A^{\cdot-} + h\nu \rightarrow A + e.$$

The efficiency curves or the curves of the relative cross-sections for the photoabstraction of electrons plotted as a function of the energy of photons make it possible to determine the threshold photon energies from which the electron affinities of the acceptors A are determined. Considerable progress has been achieved in the development of apparatus for the method and increasingly more complex ions[26-28], including aromatic ions[29], are being investigated.

Mass Spectrometry of Negative Ions

This procedure has been recently used with increasing frequency. Measurements of the appearance potentials (AP) of negative fragments under electron or photon impact permit the calculation of the electron affinities of radicals coupled with the negative ions formed[23,30,31]. The principle of this method can be described by the following equations:

(1) dissociative electron capture:

$$R_1{-}R_2 + e \rightarrow R_1^{-} + R_2^{\cdot},$$
$$EA(R_1^{\cdot}) = D(R_1 - R_2) - AP(R_1^{-}) + KE + IE;$$

(2) the formation of an ion pair:

$$R_1 - R_2 \xrightarrow{e,h\nu} (R_1{-}R_2)^{*} \rightarrow R_1^{+} + R_2^{-},$$
$$EA(R_2) = AP(R_2^{-}) - D(R_1{-}R_2) - IP(R_1^{\cdot}) - KE - IE,$$

where $D(R_1 - R_2)$ is the homolytic bond dissociation energy and KE and IE are the kinetic and internal energies of the species involved. The necessity for the determination of D, KE, IE, and IP complicates the application of this method.

A method involving the mass spectrometric investigation of the equilibria in proton transfer reactions has also been used to determine the electron affinities of organic free radicals [32].

The Method of Collision Ionisation of Alkali Metal Atoms

This procedure is promising. The electron affinities are calculated from the threshold value for the reaction

$$M + A \rightarrow M^+ + A^-,$$

where M is an alkali metal, usually caesium. The threshold value is determined by studying the dependence of the relative reaction cross-section on the translational energy of the reactants [33]. It is equal to the difference between the ionisation potential of the alkali metal and the electron affinity of the acceptor A. The method yields reliable results and has no fundamental limitations except that the process must lead to the formation of the molecular ion A^- and not its decomposition products. The accuracy of the method [34-36] does not usually exceed ±0.1 eV. Electron transfer to the acceptor can be achieved also with the aid of other electron donors with known ionisation potentials [36,37].

The Electron Capture or Thermal Equilibrium Method [15,19]

The method reduces to the investigation of the equilibria in reactions involving the capture of thermalised electrons by the acceptor in the gas phasa:

$$e + A \xrightarrow{K} A^- .$$

The steady-state concentration of electrons varies exponentially with the acceptor concentration in the system:

$$[e] = [e_0]e^{-\varkappa[A]},$$

where $\varkappa$ is the electron capture coefficient. The method is based on the determination of the electron capture coefficients. When $[e] \gg [A]$, we have $\varkappa = K$. At fairly high temperatures, $\ln \varkappa T^{3/2}$ varies linearly with $1/T$ and the slope of the straight line is EA/K. The intercept which the plot makes on the ordinate axis is not constant. It is believed that the temperature variation of $\varkappa$ is required for the correct determination of EA. At low temperatures, $\varkappa$ becomes approximately constant. Many EA values for organic compounds have also been determined using the relative [19] electron capture constant $\varkappa'$.

Thermalised electrons are obtained in the form of secondary electrons when a mixture of gases, usually of methane and argon, is irradiated. Apart from thermalised electrons, radicals and positively charged ions, whose concentration does not vary under standard conditions even when the amounts of the acceptor investigated are small, are generated. The presence of the test gas influences only the concentration of the thermalised electrons. The experimentally determined quantities are [e] and [A]. Their separate determination is based either on the different mobilities of the electron and the acceptor molecule or on the magnetron effect. The latter requires special consideration, since the method based on this effect has come to be called the "magnetron method". The method, introduced for the first time by Sutton and Mayer [38,39], has been used particularly successfully by Page and coworkers [17,40]. The experimental apparatus consists of a cathode, a grid, and an anode mounted within a solenoid. The test substance is introduced in the gaseous state (vapour pressure 10^{-4}–10^{-2} mmHg). Thermalised electrons are generated by the heated cathode. In the absence of a magnetic field, both the electrons and the radical-anions A^- reach the anode. The magnetic field forces the electrons to move along a circular orbit and they are captured by the grid. The magnetic field has little effect on the motion of A^-. Thus it is possible to measure separately the currents generated by the streams of electrons (i_e) and radical-anions (i_i). Since

$$i_e/i_i = K \cdot \exp(-EA/RT) \quad \text{and}$$

$$-\frac{R\, d\ln(i_e/i_i)}{d(1/T)} = EA(\bar{T}),$$

the slope of the straight line defined by the equation $Rd\ln(i_e/i_i) = cd(1/T)$ is equal to the electron affinity at a temperature T. The latter is determined as the average temperature of the cathode in the range where the measurements are made. The electron affinity at 0 K is obtained from the relation $EA_0 = EA(\bar{T}) - {}^3/_2 R\bar{T}$.

The method is unreliable, because the negative ion corresponding to the given species for which EA is to be determined is not identified, which may lead to erroneous results [41]. Small amounts of impurities and products of thermal reactions can also bind electrons and can lead to considerable errors.

The Method of Charge-Transfer Complexes (CTC)

It is based on the determination of the charge-transfer (CT) energy for complexes of a series of donors with the electron acceptor investigated [19]. The CT energy is usually determined from the CT band maximum. According to Mulliken's theory [5], the CT energy for a weak interaction between the donor and the acceptor can be expressed by the following equation:

$$h\nu_{CT} = IP - EA + G_0 - C + X_1 + X_0 \quad , \qquad (1)$$

where G_0 is the energy of all types of interactions between the donor and the acceptor in the ground CTC state, with the exception of the donor–acceptor interaction, C is the energy of the Coulombic interaction between the components in the excited CTC state, and X_0 and X_1 are the energies of the resonance interaction between $\psi(D, A)$ and $\psi(D^+, A^-)$ in the ground and excited CTC states.

Using the expressions for X_0 and X_1, it is possible to obtain the following equation:

$$h\nu_{CT} = IP - EA - C - G_0 + \frac{\beta_0^2 + \beta_1^2}{IP - EA - C - G_0},$$

where $\beta_0 = H_0 + S_{01}W_0$ and $\beta_1 = H_{01} - S_{01}W_1$. The latter equation may be simplified because C and G_0 can be assumed to be constant for CTCs of the same type with a fairly satisfactory degree of approximation. For a weak interaction between the donor and the acceptor, the overlap integral S_{01} is small, so that β_0 and β_1 can also be regarded as approximately constant. Thus we obtain [1]

$$h\nu_{CT} = IP - (EA + E) + \frac{C_1}{IP - (EA + E)}.$$

For small values of C_1 and fairly high ionisation potentials, this equation acquires an even simpler form, which is frequently used in investigations [1-4,42-45]:

$$h\nu_{CT} = IP - EA - W, \qquad (2)$$

where W is an approximately constant quantity for the given class of CTC.

In principle, Eqn. (2) can be used directly to calculate the electron affinities of acceptors, provided that W is known. Since its exact value is not known, one usually starts with Eqn. (2), obtaining in this way the following expression for complexes of a common donor with a series of acceptors [19]:

$$h\nu_{CT}^{x} - h\nu_{CT}^{0} = \overset{0}{EA} - EA^{x} + W^{0} - W^{x}, \quad (3)$$

where EA^0 and EA^X are the electron affinities of the reference acceptor and the test acceptor respectively.

It is frequently assumed [1-4,19] that $W^0 - W^X = 0$ and Eqn. (3) is simplified in this way is used to calculate EA^X. This is apparently justified only for acceptors having a similar structure and when, instead of a single donor, a series of donors are used in order to eliminate specific interactions of the components, since it has been shown [46] that the error resulting from the introduction of the last approximation can reach as much as 0.4 eV. Aromatic hydrocarbons, whose first and second ionisation potentials differ little in terms of energy, are most suitable as donors. *p*-Chloranil is most often employed as the reference acceptor [3,19,47].

The Method Based on the Study of the Equilibrium Between the Radical-Ion and the Neutral Molecule

It is based on the determination of the equilibrium constant for the reaction

$$A^{\mp} + B \overset{K}{\rightleftarrows} B^{\mp} + A, \quad (4)$$

using spectroscopic analytical methods for this purpose. If the medium is insufficiently polar and ion pairs are present, another equilibrium actually obtains:

$$(A^{\mp}, K^{+}) + B \overset{K'}{\rightleftarrows} (B^{\mp}, K^{+}) + A$$

$$K' = K \frac{K_{diss}\,(A^{\mp}, K^{+})}{K_{diss}\,(B^{\mp}, K^{+})},$$

where K_{diss} are the dissociation constants of the ion pairs. In solutions of radical-ions, more complex equilibria can also occur [48]. The enthalpy of reaction (4) is correlated with the difference between the values of EA for the acceptors A and B. The less well-founded equation

$$-RT \ln K' = EA\,(A) - EA\,(B).$$

is usually employed [49].

The Potentiometric Method [15]

The method is based on the measurement of the potential arising in the $A/A^{\mp}$ redox system. A modified method, resembling potentiometric titration, has found the most extensive applications. Measurements are made of the potential between two platinum electrodes, one of which is immersed in a standard redox system $A_0/A_0^{\mp}$ and the other in a solution containing the test redox system $A_X/A_X^{\mp}$. The redox system investigated is obtained by titrating a solution of A_X with a standard solution of $A_0/A_0^{\mp}$. The half-wave potential ϵ is determined from the titration curve. According to Jagur-Grodzinski et al. [50], it is given by the expression

$$\varepsilon = \varepsilon_0 + 0.03 \ln (K_{A_0}/K_{A_X}) + 0.03 \ln \frac{[A_X, K^+]_t}{[A_0, K^+]_t}$$

where ϵ_0 is the standard potential of the reaction $A_0^{\mp} + A_X \rightleftharpoons A_X^{\mp} + A_0$, K_{A_0} and K_{A_X} are the dissociation constants of the corresponding ion pairs, and $[A^{\mp}, K^+]_t$ is the sum of $(A_0^{\mp}, K^+)$ and $(A_X^{\mp}, K^+)$.

The standard potential ϵ_0 is equal to the difference between the electron affinities of A_X and A_0, i.e. the method yields the relative electron affinities. The relative electron affinities thus obtained are satisfactorily correlated with the corresponding absolute values for the gas phase, the slope of the straight line being close to unity [15].

The Polarographic Method

The reversible one-electron reduction of the acceptor A is determined by the following process:

$$A_{solv} + e \rightleftharpoons A_{solv}^{\mp} \quad .$$

The half-wave potential is given by the expression [51]

$$E_{1/2} = E_0 - \frac{RT}{F} \ln \frac{D_1}{D_2},$$

where E_0 is the formal or standard potential, R the gas constant, F the Faraday, and D_1 and D_2 are the diffusion coefficients of the oxidised and reduced forms in the layer near the electrode.

E_0 is determined by the energetic characteristics of many processes [19], including the electron affinity of the acceptor A:

$$EA = E_{1/2} - \Delta E_{solv} - 5.07 + \frac{RT}{F} \ln D_1/D_2,$$

where ΔE_{solv} is the difference between the solvation energies of $A^{\mp}$ and A.

Since the diffusion coefficients D_1 and D_2 cannot differ by more than 1-2 orders of magnitude, the last term of this equation is negligibly small and can be rejected. Consequently the relation between the electron affinity in the gas phase and the half-wave potential of the reversible one-electron reduction is given by the equation

$$EA = E_{1/2} - \Delta E_{solv} + 5.07 \text{ (eV)} \quad . \quad (5)$$

Since the solvation energies of neutral molecules are small, the quantity ΔE_{solv} is determined mainly by the solvation energy of the corresponding radical-anion, i.e. $\Delta E_{solv} \simeq E_{solv}^{A^{\mp}}$. The study of the radical-anions of aromatic hydrocarbons [19,51,52] and of other electron acceptors [19] has shown that the solvation energies of radical-anions do not vary significantly with the structure of the delocalised radical-ion. According to Briegleb [19], the differences between the values of ΔE_{solv} for a series of different electron acceptors in acetonitrile do not exceed ±0.15 eV. A change of solvent can alter the solvation energy to a greater extent and hence also the values of $E_{1/2}$. Thus, when acetone is replaced by dichloromethane [53], the values of $E_{1/2}$ for a series of different acceptors change by 0.31 ± 0.05 V, i.e. the changes in the solvation energies for different radical-ions are approximately the same on passing from one solvent to another. The following equation can therefore be used with an adequate degree of approximation to calculate the electron affinities of acceptors forming delocalised radical-ions:

$$EA \simeq E_{1/2} + C \quad ,$$

$$\Delta EA \simeq \Delta E_{1/2},$$

where C is a constant and $E_{1/2}$ the half-wave potential for polarographic reduction under the same condition.

Apart from the methods described above, other procedures are also available for the determination of electron affinities[21,54], but are not considered here.

IV. ELECTRON AFFINITIES OF NEUTRAL ELECTRON ACCEPTORS

The vast majority of experimental data have been obtained by methods which do not yield directly the absolute electron affinities, but permit their calculation, provided that one can estimate in some way the remaining unknowns in the equations used to determine EA. It is therefore not surprising that the polarographic and CTC methods lead to very different estimates of absolute electron affinities (Table 1) in studies by different investigators. If one considers relative electron affinities obtained for the same estimates of other unknowns, instead of their absolute values, the situation changes radically (Table 1) and the majority of values for a particular acceptor agree to within 0.15 eV. It is also found that the relative electron affinities are satisfactorily correlated (Figs. 2 and 3) with the absolute electron affinities obtained by independent methods (electron capture, magnetron, and mass-spectrometric methods), the slope of the straight lines being close to unity.

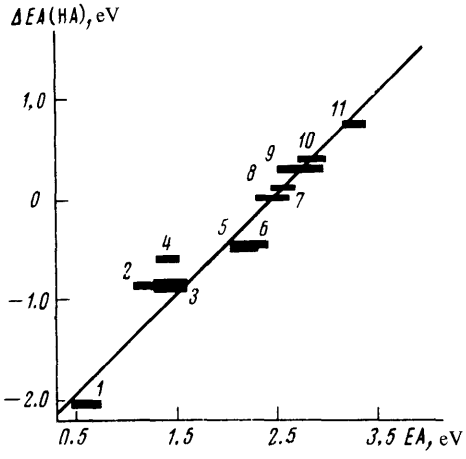


Figure 2. Relation between the relative (CTC method, reference acceptor–p-chloranil) and absolute electron affinities: 1) acceptor 45, electron capture method; 2) acceptor 144, magnetron method; 3) acceptor 11, mass spectrometric method; 4) acceptor 100, magnetron method; 5) acceptor 104, magnetron method; 6) acceptor 40, magnetron method; 7) acceptor 129, magnetron method; 8) acceptor 44, magnetron method; 9) acceptor 8, magnetron method; 10) acceptor 168, magnetron method; 11) acceptor 10, magnetron method (the acceptors are numbered in accordance with Table 1).

Consequently the problem of determining the absolute electron affinities can be solved by determining the relative electron affinities of different acceptors and by selecting the most probable absolute electron affinity of the reference acceptor–p-chloranil (HA). The absolute electron affinities of p-chloranil, obtained by the magnetron method, are also listed in Table 1. The validity of the latter results can be assessed in several ways. One of these involves the comparison of the results obtained by different methods using the relative electron affinities; the required data are presented in Table 2.

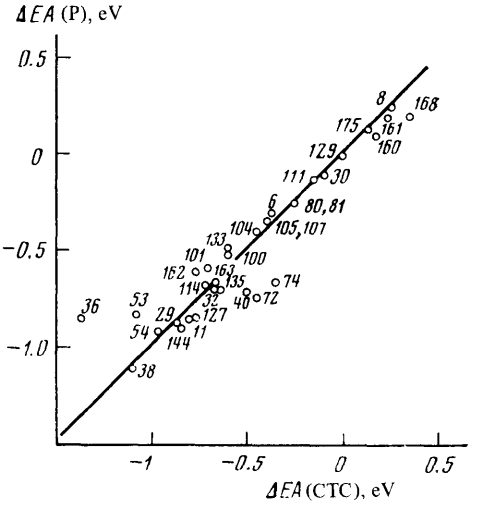


Figure 3. Comparison of the results obtained by the CTC and polarographic methods (the acceptors are numbered in accordance with Table 1).

Tbe absolute electron affinity of p-chloranil can also be inferred from a more detailed analysis of the results obtained by the polarographic method. Here the principal difficulty consists in the estimation of the solvation energies of the radical-anions arising in the one-electron reduction of the acceptor. Although much attention has been devoted to the determination of the solvation energies of charged species, their exact values are unknown[23,110,111]. This is particularly true of organic radical-anions and is the reason why the polarographic method has yielded two series[14] of electron affinities, differing by 1 eV.

One can assume with a satisfactory degree of approximation that the lower limit to the solvation energies of organic ions in polar solvents is given by the polarisation energies[9] in crystals of non-polar aromatic hydrocarbons, which are of the order[9,112] of 1.5 eV. Since the polarisation energy of negative ions is approximately 0.2 eV higher than that of positive ions and the negative charge of the radical-anions of acceptors is largely localised on the heteroatoms, one can assume that the lower limit to the solvation energies of the radical-anions of organic electron acceptors is approximately 2 eV. Since the solvation energy depends markedly on the charge density, the solvation energy of the iodide ion should probably be regarded as the upper limit, assuming that the charge is more delocalised in any organic radical-anion with a fairly well developed π-electron system. In aprotic polar solvents, incapable of specific solvation of anions, the solvation energy of the iodide ion[110,113] is approximately 2.5–3 eV. Since ΔE_{solv} is somewhat smaller than E_{solv}, it follows that, in conformity with Eqn. (5), the most probable electron affinity of p-chloranil exceeds 2.2 eV.

Table 1.

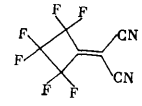
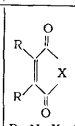
No.	Compound	*EA*, eV	ΔEA^*, eV	*EA* (abs.), eV	Method** and references
1	2	3	4	5	6
1.	Tetranitromethane 	1.8	—	1.8	EC (Ref.55)
2.	$R_1=R_2=R_3=R_4=H$	−1.8	—	—	QC (Ref.56)
3.	$R_1=COOC_2H_5$; $R_2=R_3=R_4=H$	0.25	—	0.25	EC (Ref.19
4.	$R_1=R_3=COOC_2H_5$;	0.6	—	0.6	EC (Ref.19)
	$R_2=R_4=H$ (*trans*-)	0.8±0.1	—	0.8	MM (Ref.57)
5.	$R_1=R_3=CN$; $R_2=R_4=H$	—	−0.4	2.1	CTC (Ref.19)
6.	$R_1=R_4=CN$; $R_2=R_3=COOH$	—	−0.3		P (Ref.14,58)
7.	$R_1=R_2=CN$; $R_3=R_4=CF_3$	—	−0.1	2.35	CTC (Ref.59)
		2.89±0.1	—	—	MM (Ref.57)
8.	$R_1=R_2=R_3=R_4=CN$	1.6	—	2.75	EC (Ref.60)
		—	+0.3	—	CTC (Ref.19,61)
		—	+0.34	—	CTC (Ref.62)
			+0.25	—	P (Ref.19)
9.			−0.42	2.05	CTC (Ref.59)
10.	Hexacyanobutadiene	3.3±0.1	—	3.2	MM (Ref.57)
			+0.7	—	CTC (Ref.63)
11.	 R=H, X=O	—	−0.83	—	P, CTC (Ref.19)
		1.43	—	—	QC (Ref.64)
		1.4±0.2	—	1.4	MS (Ref.65)
		—	−1.25	—	CTC (Ref.66)
12.	R=Cl, X=O	0.55	−0.8	1.65	CTC (Ref.66,67)
13.	R=I, X=O	0.45	−0.9	1.55	CTC (Ref.67)
14.	X=S, R=Cl	0.6	−0.75	1.7	CTC (Ref.68)
					
15.	R=Cl	0.4	—	0.4	EC (Ref.19)
16.	R=Br	0.4	—	0.4	EC (Ref.19)
17.	R=I	0.54	—	0.5	EC (Ref.19)
18.	R=CHO	0.43	—	0.5	EC (Ref.69,70)
		—	−1.85	—	P (Ref.71)
19.	$R=COOCH_3$	0.2	—	⩾0.2	EC
20.	R=COF	−0.42	−1.85	0.6	P (Ref.19,71)
21.	R=COCl	0.03	−1.40	⩽1.05	P (Ref.19, 71)
22.	R=COBr	0.20	−1.20	⩽1.25	P (Ref.19,71)
23.	$R=NO_2$	0.54	—	—	EC (Ref.19)
			−1.15	⩽1.3	P (Ref.72)
					
24.	$R_1=COCl$, $R_2=OCH_3$	−0.13	−1.55	⩽0.9	P (Ref.19,71)
25.	$R_1=COCl$, $R_2=CH_3$	−0.05	−1.45	⩽1.0	P (Ref.71)
26.	$R_1=COCl$, $R_2=NO_2$	0.77	−0.65	⩽1.8	P (Ref.71)
27.	$R_1=R_2=CHO$	0.21	−1.17	⩽1.3	P (Ref.71)
		0.98	—	—	QC (Ref.63)
		0.60	—	—	EC (Ref.73)
28.	$R_1=R_2=COCl$	0.52	−0.9	⩽1.55	P (Ref.71)
29.	$R_1=R_2=COBr$	0.54	−0.9	1.55	P (Ref.71)
30.	$R_1=R_2=COCH_3$	0.64	—	0.65	EC (Ref.73)
		0.95	−0.47	0.9	P, CTC (Ref.71)
31.	$R_1=R_2=CN$	—	−1.65	—	P (Ref.74)
32.	$R_1=R_2=NO_2$	—	−0.7		P (Ref.75)
		0.7	−0.67	⩽1.75	CTC (Ref.19)
33.	$R_1=Cl$ $R_2=NO_2$	—	−1.1	1.35	P (Ref.75)
					
34.	$R_1=R_2=COCH_3$	0.55	—	⩾0.55	EC (Ref.73)
35.	$R_1=R_2=CN$	1.1±0.13	—	1.1	MM (Ref.57)
36.	$R_1=R_2=NO_2$	—	−0.84	⩽1.6	P (Ref.75)
					
37.	$R_1=R_2=COCH_3$	0.55	—	0.55	EC (Ref.73)
38.	$R_1=R_2=NO_2$	—	−0.9	—	P (Ref.75)
		0.3	−1.1	—	CTC (Ref.19)
		1.5	−1.1	1.35	P (Ref.58)
		—	−1.1	—	CTC (Ref.76)
		—	−1.2	—	CTC (Ref.77)
					
39.	$R_1=R_3=R_5=CN$; $R_2=R_4=R_6=H$	0.1	−1.27	1.25	CTC (Ref.19)
		—	−1.20		CTC (Ref.78)
40.	$R_1=R_2=R_4=R_5=CN$; $R_3=R_6=H$	—	−0.71	—	P (Ref.79)
		0.4	−0.97	—	CTC (Ref.19)
		2.19±0.2	—	2.0	MM (Ref.57)
		2.15	—	—	MM (Ref.17)

Table 1 (cont'd.)

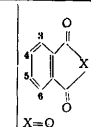
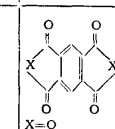
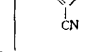
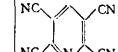
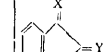
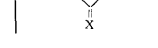
No.	Compound	*EA*, eV	ΔEA^*, eV	*EA* (abs.), eV	Method** and references
1	2	3	4	5	6
41.	$R_1=R_2=CN$; $R_3=R_4=R_5=R_6=Cl$	—	−1.0	1.45	CTC (Ref.78
42.	$R_1=R_3=R_5=CN$; $R_2=R_4=CH_3$	—	−0.8	1.65	CTC (Ref.80)
43.	R_1 to $R_5=CN$; $R_6=CH_3$	—	−0.3	2.15	CTC (Ref.80)
44.	R_1 to $R_6=CN$	2.55	—	—	QC (Ref.64)
		2.55	—	2.55	MM (Ref.57)
		—	+0.1	—	CTC (Ref.89)
45.	R_1 to $R_6=Cl$	0.58	—	⩾0.6	EC (Ref.19)
46.	R_1 to $R_6=F$	—	−2.05	⩾0.4	CTC (Ref.81)
47.	$R_1=R_4=COCH_3$; $R_2=R_3=R_5=R_6=Cl$	0.77	—	0.8	EC (Ref.73)
48.	$R_1=R_4=NO_2R_2=CH_3$; $R_3=R_5=R_6=H$	—	−1.27	1.2	CTC (Ref.19)
49.	$R_1=R_3=NO_2R_5=F$; $R_2=R_4=R_6=H$	—	−0.9	1.55	P (Ref.75)
50.	$R_1=R_3=NO_2R_2=R_4=F$; $R_5=R_6=H$	—	−0.85	1.60	P (Ref.75)
51.	$R_1=R_3=NO_2R_2=OH$; $R_4=R_5=R_6=H$	0.6	—	⩾0.6	EC (Ref.19)
52.	$R_1=R_3=R_5=NO_2$; $R_2=R_4=R_6=H$	—	−0.6	1.75	P (Ref.75)
		0.7	−0.7	—	P, CTC (Ref.19)
		1.86	−0.74		P (Ref.58)
		2.63	—	—	MM (Ref.17)
		—	−0.75	—	CTC (Ref.62)
53.	$R_1=R_3=R_5=NO_2$;	1.78	−0.82	1.4	P (Ref.58)
	$R_2=OCH_3$; $R_4=R_6=H$	—	−1.08		CTC (Ref.82)
					CTC (Ref.19)
54.	$R_1=R_3=R_5=NO_2$;	0.6	−0.77		P (Ref.58)
	$R_2=CH_3$; $R_4=R_6=H$	1.69	−0.9	1.55	P (Ref.58)
55.	$R_1=R_3=R_5=NO_2$;	1.7	−0.9	1.95	CTC (Ref.86)
	$R_2=Cl$; $R_4=R_6=H$	—	−0.45	—	CTC (Ref.84)
56.	$R_1=R_3=R_5=NO_2$;	—	−0.25	2.2	
	$R_2=CN$; $R_4=R_6=H$				
57.	$R_1=R_3=R_5=NO_2$	—	−0.97	1.45	CTC (ref.19)
					
58.	X=O	0.1	−1.3	1.15	P (Ref.19)
59.	X=S	0.38	−1.0	⩽1.45	CTC (Ref.68)
60.	X=O 3,4,5,6-tetrachloro-	0.55	−0.82	—	CTC (Ref.19)
		—	−0.85	1.65	CTC (Ref.78)
		1.8	−0.8	—	P (Ref.58)
61.	X=O; 3,5-dinitro-	—	−0.34	2.1	CTC (Ref.85)
62.	X=NH	1.5	−1.1	1.35	P (Ref.70)
					
63.	X=O	0.8	−0.55	1.9	P, CTC (Ref.19)
64.	X=O, dibromo-	1.15	−0.32	2.15	P, CTC (Ref.19)
65.	X=S	—	−0.95	1.5	CTC (Ref.68)
66.		—	−0.25	2.2	CTC (Ref.78)
67.		2.18±0.07	—	2.2	MM (Ref.37)
					
68.	X=Y=O	—	−0.3	2.15	CTC (Ref.86)
69.	X=O; Y=C(CN)$_2$	—	0	2.45	CTC (Ref.86)
70.	X=C(CN)$_2$; Y=O	—	+0.2	2.65	CTC (Ref.86)
					
71.	R=R$_1$=CF$_3$	—	+0.15	2.60	CTC (Ref.87)
72.	R=R$_1$=Ph	—	−0.45	1.85	CTC (Ref.86)
			−0.75	—	P (Ref.88)
73.	R=C$_6$H$_5$OCO; R$_1$=Ph	—	−0.35	1.95	CTC (Ref.87)
74.	R=Ph; R$_1$R$_1$= 	—	−0.35	1.95	CTC (Ref.87)
		—	−0.65	—	P (Ref.88)
75.	R=C$_2$H$_5$OCO R$_1$R$_1$= 	—	−0.15	2.15	CTC (Ref.87)
	 X=O				

Table 1 (cont'd.)

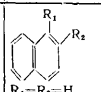
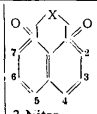
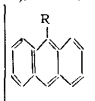
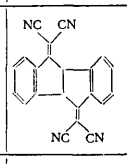
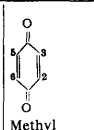
No.	Compound	*EA*, eV	ΔEA^*, eV	*EA* (abs.), eV	Method** and references
1	2	3	4	5	6
76.	2,7-Dinitro-	—	−0.65	1.85	P (Ref.89)
77.	3,6-Dinitro-	—	−0.53	1.95	P (Ref.89)
78.	2,4,7-Trinitro-	—	−0.45	2.05	P (Ref.89)
		—	−0.3	—	CTC (Ref.19)
79.	2,4,5,7-Tetranitro- X=C(CN)$_2$	—	−0.25	2.2	P (Ref.89)
80.	2,4-Dinitro-	—	−0.25	2.2	P, CTC (Ref.89)
81.	2,5-Dinitro-	—	−0.25	2.2	P, CTC (Ref.89)
82.	2,6-Dinitro-	—	−0.2	2.25	CTC (Ref.89)
83.	2,7-Dinitro-	—	−0.25	2.2	CTC (Ref.89)
84.	3,6-Dinitro-	—	−0.15	2.3	CTC (Ref.89)
85.	2,4,7-Trinitro-	—	0	2.45	CTC (Ref.89)
		—	+0.1	—	CTC (Ref.90,91)
86.	2,4,5,7-Tetranitro-	—	+0.1	2.55	CTC (Ref.89)
					
87.	R_1=R_2=H	0.15	—	0.15	EC (Ref.92)
88.	R_1=COH; R_2=H	0.67	—	0.7	EC (Ref.92)
89.	R_2=COH; R_1=H	0.62	—	0.6	EC (Ref.92)
	 X=O				
90.	3-Nitro-	—	−0.67	1.8	CTC (Ref.93,94)
91.	4-Nitro-	—	−0.67	1.8	CTC (Ref.93)
92.	3,6-Dinitro-	—	−0.37	2.1	CTC (Ref.93)
93.	4,5-Dinitro-	—	−0.27	2.2	CTC (Ref.93)
94.	2,4,5,7-Tetranitro- X=NC$_2$H$_5$	—	+0.4	2.85	CTC (Ref.93
95.	3,6-Dinitro-	—	−0.55	1.9	CTC (Ref.93)
96.	4,5-Dinitro-	—	0.45	2.0	CTC (Ref.93)
					
97.	R=H	0.57	—	0.6	EC (Ref.95)
98.	R=COH	1.0	—	1.0	EC (Ref.69)
99.		—	+0.1	2.55	P (Ref.96)
100.		1.4	—	1.85	MM (Ref.14,97)
		1.94	—		QC (Ref.64)
		0.64	—		EC (Ref.19)
			−0.60		CTC (Ref.19)
			−0.52		P (Ref.19)
			−0.7		CTC (Ref.3)
101.	Methyl	—	−0.71	1.75	CTC (Ref.19)
		—	−0.6		P (Ref.19)
102.	Methoxy-	—	−0.63	1.70	P (Ref.70)
103.	Dimethylamino-	—	−0.76	1.60	P (Ref.70)
104.	Fluoro-	2.16	—	2.05	MM (Ref.17)
		—	−0.45		CTC (Ref.14,19)
		—	−0.39		P (Ref.70)
105.	Chloro-	—	−0.35	2.05	P (Ref.19)
		—	−0.37		CTC (Ref.19)
106.	Bromo-	—	−0.37	2.05	P (Ref.19)
107.	Iodo-	—	−0.4	2.05	CTC (Ref.19)
108.	Methoxycarbonyl	—	−0.40	2.05	CTC (Ref.70)
109.	Acetyl-	—	0.32	—	P (Ref.70)
		—	−0.32	2.1	CTC (Ref.19)
		—	−0.4	—	CTC (Ref.70)
110.	Trifluoromethyl	—	−0.25	2.2	CTC, P (Ref.70)
111.	Cyano-	—	−0.15	2.3	CTC (Ref.19)
		—	−0.15	—	P, CTC (Ref.70)
112.	Nitro-	—	+0.1	2.55	P, CTC (Ref.70)
		—	+0.1	—	CTC (Ref.19)
113.	Phenyl-	—	−0.50	1.95	P, CTC (Ref.70)
114.	2,6-Dimethyl-	—	−0.77	1.65	CTC (Ref.19)
115.	2,6-Dichloro-	—	−0.17	—	CTC (Ref.19)
		—	−0.19	2.25	P (Ref.19)
116.	2,6-Dibromo-	—	−0.2	2.25	CTC (Ref.19)
117.	2,6-Dicyano-	—	+1.0	⩽3.4	CTC (Ref.98)
118.	2,6-Dinitro-	—	+0.38	2.85	CTC (Ref.19)
119.	2,5-Dimethyl-	—	−0.7	1.75	P, CTC (Ref.19)
120.	2,5-Di-t-butyl	—	−0.51	1.95	P (Ref.19)
121.	2,5-Dichloro-	—	−0.22	2.25	CTC (Ref.19)
		—	−0.19		P (Ref.19)
122.	2,5-Dicyano-	—	+0.3	2.75	CTC (Ref.98)
123.	2,3-Dichloro-	—	−0.27	2.2	CTC (Ref.19)

Table 1 (cont'd.)

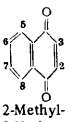
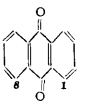
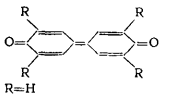
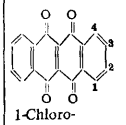
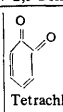
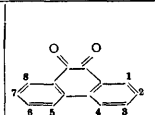
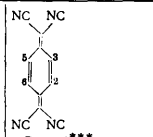
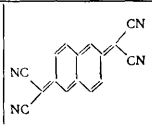
No.	Compound	*EA*, eV	ΔEA^*, eV	*EA* (abs.), eV	Method** and references
1	2	3	4	5	6
124.	2,3-Dicyano-	—	+0.33	2.75	CTC (Ref.19)
		—	+0.26	—	CTC (Ref.3)
		—	+0.38	—	CTC (Ref.49)
125.	2,3,5-Trimethyl-	—	−0.7	1.75	CTC (Ref.19)
126.	2,3,5-Trichloro-	—	−0.1	2.35	P, CTC (Ref.19)
127.	Tetramethyl	—	−0.80	1.65	P, CTC (Ref.19)
128.	3,5,6-Trifluoro-2-methyl	—	−0.25	2.2	P, CTC (Ref.70)
129.	Tetrachloro-(HA)	2.4	—	2.45	MM (Ref.17)
		2.46	—	—	MM (Ref.46)
		2.59	—	—	MM (Ref.46,99)
		2.05	—	—	MM, CTC (Ref.100)
130.	Tetrabromo-	—	0	2.45	P, CTC (Ref.19)
131.	Tetrafluoro-	—	−0.05	2.4	P (Ref.102)
132.	Tetraiodo-	—	0	2.45	P, CTC (Ref.19)
133.	2,3-Dichloro-5,6-dicyano-	—	+0.54	3.0	CTC (Ref.60)
		—	+0.58	—	CTC (Ref.19)
		—	+0.5	—	P (Ref.19)
		—	+0.62	—	CTC (Ref.49)
134.	Tetracyano-	—	+0.43	3.40	CTC (Ref.19)
		—	+0.97	—	CTC (Ref.80,98)
135.		—	0.6	1.75	CTC (Ref.87)
		—	−0.67	—	CTC (Ref.19)
		—	−0.72	—	P (Ref.19)
		1.6	—	—	QC (Ref.64)
136.	2-Methyl-	—	−0.75	1.7	P (Ref.14)
137.	2-Hydroxy-	—	−0.82	1.65	CTC (Ref.19)
138.	5-Hydroxy-	—	−0.5	1.9	P, CTC (Ref.19)
139.	2-Amino-	—	−0.93	1.5	P (Ref.19)
140.	2,3-Dichloro-	—	−0.40	2.05	CTC (Ref.46)
141.	2,3-Dichloro-5-nitro-	—	−0.22	2.25	CTC (Ref.46)
142.	2,3-Dicyano-	—	+0.28	2.70	CTC (Ref.46)
143.	2,3-Dicyano-5-nitro	—	+0.33	2.80	CTC (Ref.46)
144.		—	−0.87	1.55	CTC (Ref.19)
		—	−0.8	—	CTC (Ref.87)
		—	−0.95	—	P (Ref.19)
		1.15	—	—	MM (Ref.14)
145.	1-Hydroxy-	—	−0.67	1.75	CTC (Ref.19)
		—	−0.78	—	P (Ref.19)
146.	1,8-Dihydroxy-	—	−0.5	1.95	CTC (Ref.19)
147.	1,4-Anthraquinone	—	−0.76	1.7	P (Ref.102)
148.	5,12-Tetracenequinone	—	−0.9	1.55	CTC (Ref.87)
149.	6,13-Pentacenequinone	—	−1.05	1.40	CTC (Ref.87)
					
150.	R=H	—	−0.25	2.20	P (Ref.102)
151.	R=Cl	—	+0.34	2.8	CTC (Ref.103)
152.	R=Br	—	+0.36	2.8	CTC (Ref.103)
153.		—	+0.05	2.5	CTC (Ref.104)
154.	1-Chloro-	—	+0.05	2.5	CTC (Ref.105)
155.	2-Chloro-	—	+0.15	2.6	CTC (Ref.105)
156.	2-Methoxy-	—	+0.05	2.5	CTC (Ref.105)
157.	1,2,3,4-Tetrachloro-	—	+0.05	2.5	CTC (Ref.105)
158.	2,3-Benzo-	—	0	2.45	CTC (Ref.105)
159.		—	−0.32	2.15	P (Ref.102)
160.	Tetrachloro-	—	+0.18	2.6	CTC (Ref.19)
		—	+0.1	—	P (Ref.19)
161.	Tetrabromo-	—	+0.23	2.65	CTC (Ref.19)
		—	+0.2		P (Ref.19)
162.	3,4-Benzo-	—	−0.77	1.85	CTC (Ref.19)
		—	−0.6	—	P (Ref.102)
		1.55	—	—	QC (Ref.64)
163.		—	−0.67	1.75	CTC (Ref.19,14)
		—	−0.67	—	P (Ref.19)
164.	3,6-Dinitro-	—	−0.15	2.3	CTC (Ref.14)
		—	−0.2	—	P (Ref.14)
165.	2,7-Dinitro-	—	−0.2	2.25	CTC (Ref.14)
		—	−0.30	—	P (Ref.14)
166.	2,5-Dinitro-	—	−0.25	2.20	CTC (Ref.14)
		—	−0.35	—	P (Ref.14)
167.	2,4,7-Trinitro-	—	−0.1	2.35	P, CTC (Ref.14)

Table 1 (cont'd.)

No.	Compound	EA, eV	ΔEA*, eV	EA (abs.), eV	Method** and references
1	2	3	4	5	6
168.		2.8±0.1	—	2.8	MS (Ref.106)
		—	+0.35		CTC (Ref.19)
		—	+0.20	—	P (Ref.19)
		2.88±0.2	—	—	MM
169.	n-Propyl***	—	+0.12	—	P (Ref.107)
		—	+0.1	2.8	P (Ref.107)
170.	2,5-Dimethyl	—	+0.01	2.7	P (Ref.107)
171.	2,5-Di-isopropyl	—	+0.11	2.8	P (Ref.107)
172.	2,5-Dicyano-	—	+0.60	3.3	P (Ref.107)
173.	Tetrafluoro-	—	+0.50	3.2	P (Ref.107)
174.	2,5-Dicyano-3,6-difluoro-	—	+0.74	3.4	P (Ref.107)
175.	2,3-Benzo-	—	+0.13	2.7	P, CTC (Ref.108)
176.		—	+0.2	2.9	P (Ref.109)

*ΔEA = EA(X) - EA(HA), where EA(X) and EA(HA) are the electron affinities of the test acceptor and *p*-chloranil respectively, determined by the same method.

**QC = quantum-mechanical calculation; EC = electron capture; MM = magnetron method; CTC = charge-transfer complex method; P = polarography; MS = mass spectrometry.

***For acceptors 169–176, the values of EA(abs.) were estimated from the $E_{1/2}$ using tetracyanoquinodimethane as the reference acceptor.

The CTC method constitutes yet another possibility for an approximate estimation of the absolute electron affinity of *p*-chloranil. It is assumed[5] that Eqn. (1) can be simplified to the following expression with a satisfactory degree of approximation for weak $\pi-\pi$ complexes:

$$EA = IP - h\nu_{CT} + g_1 + x_1. \quad (6)$$

Table 2. Estimation of the electron affinities of *p*-chloranil relative to the absolute electron affinities of other electron acceptors.

Acceptor	EA, eV	Method of determination of EA	$\Delta EA = EA$ (X) − EA (HA), eV	EA (HA), eV
Hexachlorobenzene	0.55	EC	−2.05	2.6
Benzaldehyde	0.43	EC	−1.85	2.3
Naphthalene	0.15	EC	−2.45	2.6
Anthracene	0.57	EC	−1.95	2.5
Maleic anhydride	1.4±0.2	MS	0.85	2.25±0.2
7,7',8,8'-Tetracyano-quinodimethane	2.88±0.2	MM	0.37	2.50±0.2
	2.80±0.1	MS	0.37	2.43±0.1

*CT and CTC methods of determination.
**EA_{av}(HA) = 2.45 eV.

The first of the two unknowns g_1 and x_1 makes the greatest contribution, which in the case of $\pi-\pi$ complexes consist entirely of the Coulombic interaction energies (C) between the oppositely charged radical-ions in the excited CTC state. The latter can be estimated and then, using Eqn. (6) in the form

$$EA \geqslant IP - h\nu_{CT} - C, \quad (7)$$

the absolute electron affinities of the acceptors can be inferred. Several models have been used to estimate C.[3,19,114] The model of point charges at the centres of the donor and acceptor molecules must be regarded as the least satisfactory approximation. The use of localised charge models[5,114] showed that the average values of C for $\pi-\pi$ complexes are of the order of 3.3 eV. It follows from Eqn. (6) that EA(HA) ≥ 2.3 eV.

Another method for the determination of the absolute electron affinities of π-electron acceptors may be used on a comparison of the CT energies of their complexes with the CT energies of CTC acceptors of halogen atoms. Comparison of the results of the study of CTC of acceptors differing so greatly may appear incorrect at first sight. However, the characteristics of the complexes belonging to these groups are extremely similar. Thus the enthalpies of formation of the benzene–iodine[114,115] and *o*-xylene–iodine[116] complexes are 0.09 and −0.19 eV respectively. The distances between the components in the CTC of π-electron donors[115,116] are as follows: 3.36 Å for Br_3^- complexes[61] and 3.7 Å for I_3^- complexes[117]. All these characteristics are within the limits of the corresponding characteristics of the $\pi-\pi$ complexes[3]. Consequently the stabilisation energies of the excited CTC states of the $\pi-\pi$ and π-halogen atom complexes should not differ greatly and the differences between the CT energies (in the presence of a common donor) are approximately equal to the differences between the electron affinities. The electron affinities of the Br_3^- and I_3^- acceptors are known fairly well, although the data quoted by different workers[118] vary somewhat: 3.38–3.55 eV for Br_3^- and 3.08–3.25 eV for I_3^-. According to Buchel'nikova[21], higher values should be used: 3.66 and 3.29 eV. The relevant data are presented in Table 3.

Table 3. Estimation of the electron affinity of *p*-chloranil.

Donor	Acceptor				$h\nu_{CT}$(X) − $h\nu_{CT}$(HA), eV	EA (HA), eV**
	Br_3^-		HA (3)			
	$h\nu_{CT}$, eV	solvent	$h\nu_{CT}$, eV	solvent		
Benzene	2.21–2.32	Benzene (Ref.119)	3.71	CCl_4	−1.39 – −1.50	2.2–2.3
Toluene	2.15	Toluene (Ref.119)	3.25	CCl_4	−1.10	2.56
Naphthalene	1.82		2.61	CCl_4	−0.80	2.86
	I_3^-					
Benzene	2.48–2.67	Benzene (Ref.119)	3.71	CCl_4	−1.03 – −1.23	2.2–2.3
Benzene	2.88	In gas phase (Ref.12)	3.90*	In gas phase	−1.0	2.3
Toluene	2.39–2.41	Toluene (Ref.119)	3.25	CCl_4	0.85	2.44
o-Xylene	2.18	*o*-Xylene (Ref.119)	3.06	CH_2Cl_2	0.88	2.41
Mesitylene	2.10	Mesitylene (Ref.119)	2.89	CH_2Cl_2	0.79	2.50

*The polarisation energy was used[121].
**EA_{av}(HA) = 2.45 eV.

The data in Tables 1–3 show that the most probable value of the absolute electron affinity of *p*-chloranil is 2.45 ± 0.15 eV. It has been used to calculate the electron affinities of the acceptors for the determination of which there are no data obtained by absolute methods and to refine the electron affinities of the acceptors for which such data are available [Table 1, the values of EA(abs.)].

Comparison of the results obtained by different methods (Figs. 2 and 3) makes it possible in its turn to infer the errors; they do not appear to exceed 0.2 eV and in those cases where reliable results found by several methods are available, the error is much smaller.

It is well known that the introduction of substituents can alter greatly the electron affinity. The amino-, methoxy-, and alkyl groups reduce electron affinities, while the nitro-, cyano-, acyl, and alkoxycarbonyl groups as well as halogens increase them. The problem of the possible utilisation of the increments due to various substituents has remained unresolved due to the inaccuracy of the EA values themselves [19]. Nevertheless the employment of empirical increments for substituents would provide the easiest and possibly the most accurate method at the present time for the estimation of the electron affinity of a compound, since quantum-mechanical calculations for large systems with heteroatoms by the Hückel and PPP methods using the Koopmans theorem do not yield reliable results.

The increments due to substituents may be determined by comparing the affinities of the monosubstituted and unsubstituted compounds. We adopted *p*-benzoquinone as the standard system, since a fairly large number of monosubstituted *p*-benzoquinones have been investigated (Table 1, acceptors Nos. 100–113) and the following increments were obtained: –0.15 eV (CH_3O); –0.05 eV (CH_3); +0.13 eV (F); +0.18 eV (Cl); + 0.19 eV (Br); +0.17 eV (I); +0.20 (CH_3OCO); +0.25 eV (CH_3CO); +0.30 eV (CF_3); +0.43 eV (CN); +0.70 eV (NO_2).

The electron affinities of polysubstituted acceptors can be calculated from the general equation

$$EA = EA_0 + C_1 \sum_n I_n - C_2 C_1 \sum_n I_n,$$

where EA_0 is the electron affinity of the initial unsubstituted acceptor, C_1 a coefficient characterising the sensitivity of the given system to the introduction of substituents, which is determined from measurements for monosubstituted compounds and is unity for *p*-benzoquinones, I are the increments of the substituents, and C_2 is a coefficient taking into account the effects of the interaction of the substituents, i.e. the non-additivity in the case of polysubstituted compounds; for monosubstituted compounds, $C_2 = 0$.

It was found that $C_2 = 0.1$ for polysubstituted *p*-benzoquinones and remains constant for a series of other compounds, i.e. the equation for the calculation of the electron affinities of polysubstituted acceptors can be formulated as follows:

$$EA = EA_0 + 0.9C \sum_n I_n \,. \qquad (8)$$

Eqn. (8) and the above series of increments can be used without modification to estimate the electron affinities only in those systems where the effects of the substituents in different positions are approximately the same and the introduction of a new substituent does not alter appreciably the steric structure of the acceptor molecule (the substituent has a small steric effect). Such systems proved to be the derivatives of fluorenone (Table 1, Nos. 76–79) and dicyanomethylenefluorene (Nos. 80–86 with $C_1 = 0.25$), 1,4-naphthoquinone ($C_1 = 0.29$ for substituents in the 5-, 6-, 7-, and 8-positions, and $C_1 = 1.08$ for substituents in the 2- and 3-positions; Nos. 135–143), 7,7′,8,8′-tetracyanoquinodimethane ($C_1 = 0.63$; Nos. 168–174), the anhydride of phthalic acid ($C_1 = 0.75$; Nos. 11–13), *o*-benzoquinone ($C_1 = 0.7$; Nos. 159–161), diphenoquinone ($C_1 = 0.92$; Nos. 150–152), trinitrobenzene with electron-accepting substituents (with small steric effects; $C_1 = 1.1$; Nos. 52, 55, and 56), and ethylene ($C_1 = 1.9$; Nos. 3, 4, 5, 7, and 8).

Among the 45 compounds for which tests were made, the discrepancy between the experimental and calculated electron affinities did not exceed ±0.05 eV for 34 compounds and ±0.1 eV for 8 compounds, exceeding 0.1 eV for only three compounds. This shows that equations of this kind are very promising for the specific synthesis of new electron acceptors. Eqn. (8) also makes it possible to estimate the electron affinities of the unsubstituted initial compounds. A fairly unexpected result is obtained for ethylene: $EA = 0.2$ eV.

An increase of the π-electron system of the acceptor leads to a decrease of the electron affinity, despite the fact that in systems without heteroatoms the opposite behaviour is observed. This shows that, in systems with heteroatoms (they are all powerful electron acceptors), the lowest vacant molecular orbital is to a large extent localised in the part of the molecule which is directly linked to the heteroatom and its additional delocalisation leads to an increase of its energy. Thus the changes observed on passing from maleic anhydride (Table 1, No. 11) to phthalic anhydride (No. 58) and from 7,7′,8,8′-tetracyanoquinodimethane (No. 168) to 11,11′,12,12′-tetracyano-1,4-naphthoquinodimethane (No. 175) are associated with a decrease of the electron affinity by 0.25 and 0.2 eV respectively. In the series of *ortho*-quinones (No. 159, 162, and 163), an increase of the system by one benzene ring reduces the electron affinity on average by 0.2 eV. The linear condensation of benzene rings in *p*-benzoquinone derivatives (Nos. 100, 135, 144, 147, 148, 149) leads to a decrease of the electron affinity on average by 0.1–0.15 eV (per benzene ring) and this behaviour holds satisfactorily throughout the series. On the other hand, an increase of the conjugated π-electron system between the electron-accepting groups leads to an increase of electron affinity (see Nos. 168 and 176).

The replacement of the carbonyl group by the dicyanomethylene group increases electron affinity by 0.25–0.45 eV (Table 1, Nos. 68, 69, 70, 76, 83, 77, 84, 78, 85; 79, 86; 100, 168, 135, 175). In quinonoid systems, the increase is a maximum and is close to 0.45 eV for each dicyanomethylene group (Nos. 100, 168; 135, 175).

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