Polarographic reduction of some Schiff bases in dimethylformamide

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The half-wave potentials of a series of Schiff bases of the type ArCH=NAr′, where Ar and Ar′ are unsubstituted aryl groups, have been measured in dimethylformamide. The effect of structural variations of the aryl groups Ar and Ar′ on these potentials have been calculated by the linear combination of molecular orbitals (l.c.m.o.) variant of the Hückel molecular orbital (H.m.o.) theory without specific consideration of the nitrogen heteroatom present in these compounds. It is demonstrated that the equation which relates $E_{1/2}$ for the first electron transfer to theoretical quantities calculated by the l.c.m.o. theory can be applied to the data in several ways, one of which shows an interesting analogy with the Hammett σ–ρ treatment of linear free energy relationships.

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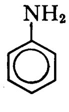
INTRODUCTION

Since its conception, the H.m.o. theory (1) has provided organic chemists with an increasingly useful tool for the interpretation of a wide variety of the physical and chemical properties of aromatic molecules. The present communication is concerned with the polarographic reduction of 24 Schiff bases of the type ArCH=NAr′ derived from the amines (I, II, III, and IV) and aldehydes (V, VI, VII, VIII, IX, and X) and the application of the linear combination of molecular orbitals (l.c.m.o.) modification of the Hückel orbital method (H.m.o.) method to the effect of structural variations of Ar and Ar′ on the half-wave potentials associated with the first electron transfer.



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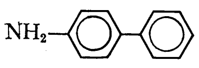

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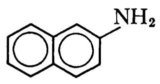

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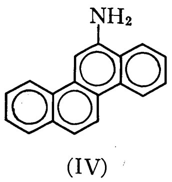

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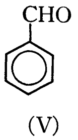

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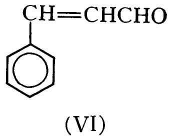

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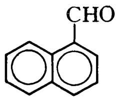

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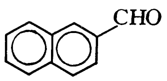

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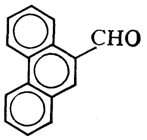

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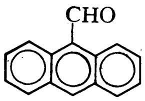

(X)

EXPERIMENTAL

Preparation of Schiff Bases

Apart from benzanil (PhCH=NPh), which was kindly donated by Dr. A. Kentaro Hoffmann of these laboratories, the Schiff bases were prepared by dissolving the appropriate amine (0.01 *M*) and aldehyde (0.01 *M*) in absolute alcohol or dimethoxyethane (ca. 20 ml) and boiling the resulting solution for a short time (ca. 15 min). On cooling, the Schiff base separated in a fairly pure state. Each specimen was then crystallized at least twice from an appropriate solvent. Further data on the substances so prepared is given in Table I.

Polarography

Purification of Dimethylformamide (DMF)

Dimethylformamide was purified essentially as described by Wawzonek *et al.* (2). On distillation only the center cut was collected, amounting to 50% of the total charge. It had b.p. 152 °C at 760 mm. Storage and handling of the solvent in a dry box, continuously flushed with dry nitrogen, proved advantageous. The small anodic wave (amine?) appearing between +0.1 and +0.3 V vs. standard calomel electrode (s.c.e.) remained virtually constant for up to at least 4 weeks storage time. Excluding this anodic wave, the residual current amounted to 0.6 μA, at most, over the range +0.1 to −2.8 V vs. s.c.e.

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TABLE I

Data relating to Schiff bases derived from aniline, 4-aminobiphenyl, 2-aminonaphthalene, and 6-aminochrysene

	Structure			Analysis			Melting points (°C)		
No.	ArNH$_2$	ArCHO	Formula, molecular weight	Atom	Required or calcd. (%)	Found (%)	Found	Literature (Ref.)	Solvent and crystal color and form
					From aniline				
1	I	V	$C_{13}H_{11}N$ 181.226	C H N	86.15 6.12 7.73	86.15 6.12 8.01	53–54	53 (22)	Light petroleum (b.p. 40–60), pale-yellow plates
2	I	VI	$C_{15}H_{13}N$ 207.262	C H N	86.92 6.32 6.76	87.16 6.02 6.56	114	109 (23)	Benzene, pale-orange prisms
3	I	VII	$C_{17}H_{13}N$ 231.28	C H N	88.28 5.67 6.06	88.48 5.57 6.12	70	71 (22)	Absolute alcohol, pale-yellow prisms
4	I	VIII	$C_{17}H_{13}N$ 231.28	C H N	88.28 5.67 6.06	— — 6.14	115	116 (22)	Absolute alcohol, very pale-yellow plates
5	I	IX	$C_{21}H_{15}N$ 281.34	C H N	89.65 5.37 4.98	89.57 5.19 4.94	120–123	—	Benzene – light petroleum (b.p. 40–60), lemon-yellow rosettes
6	I	X	$C_{21}H_{15}N$ 281.34	C H N	89.65 5.37 4.98	89.55 5.17 4.99	113–115	175(?) (24)	Absolute alcohol, bright lemon-yellow needles
					From 4-aminobiphenyl				
7	II	V	$C_{11}H_{15}N$ 257.34	C H N	88.68 5.88 5.44	88.78 5.88 5.19	146–147	—	Absolute alcohol, pale-orange plates
8	II	VI	$C_{21}H_{17}N$ 283.38	C H N	89.01 6.05 4.94	89.22 5.84 4.79	193	—	Dimethoxyethane, very small lemon-yellow blades
9	II	VII	$C_{23}H_{17}N$ 307.39	C H N	89.87 5.58 4.56	89.94 5.70 4.79	108–110	—	Dimethoxyethane, yellow plates
10	II	VIII	$C_{23}H_{17}N$ 307.39	C H N	89.87 5.58 4.56	89.82 5.51 4.77	179–181	—	Dimethoxyethane. yellow plates
11	II	IX	$C_{27}H_{19}N$ 357.45	C H N	90.72 5.36 3.92	90.52 5.06 4.11	152	—	Dimethoxyethane – absolute alcohol, bright-yellow plates
12	II	X	$C_{27}H_{19}N$ 357.45	C H N	90.72 5.36 3.92	90.91 5.59 4.16	184–185	—	Dimethoxyethane – absolute alcohol, bright-orange blades
					From 2-aminonaphthalene				
13	III	V	$C_{17}H_{13}N$ 231.282	C H N	88.28 5.67 6.06	— — 6.18	101	102 (22)	Absolute alcohol, pale-yellow plates
14	III	VI	$C_{19}H_{15}N$ 257.318	C H N	88.68 5.88 5.44	88.91 5.72 5.44	122–123	124 (25)	Dimethoxyethane, lemon-yellow plates
15	III	VII	$C_{21}H_{15}N$ 281.338	C H N	89.65 5.37 4.98	89.40 5.09 5.01	90–91	90 (22)	Dimethoxyethane – absolute alcohol, tiny yellow prisms

TABLE I (*Concluded*)

	Structure		Formula, molecular weight	Analysis			Melting points (°C)		
No.	$ArNH_2$	ArCHO		Atom	Required or calcd. (%)	Found (%)	Found	Literature (Ref.)	Solvent and crystal color and form
16	III	VIII	$C_{21}H_{15}N$	C	89.65	89.65	174–176	178	Absolute alcohol, pale-yellow plates
				H	5.37	5.35		(22)	
			281.338	N	4.98	5.00			
17	III	IX	$C_{25}H_{17}N$	C	90.61	90.74	152–154	—	Dimethoxyethane, small bright-lemon-yellow blades
				H	5.71	5.35			
			331.384	N	4.23	4.23			
18	III	X	$C_{25}H_{17}N$	C	90.61	—	145–147	—	Dimethoxyethane, yellow needles
				H	5.71	—			
			331.384	N	4.23	4.05			
				From 6-aminochrysene					
19	IV	V	$C_{25}H_{17}N$	C	90.61	90.55	160–161	—	Dimethoxyethane, lemon-yellow needles
				H	5.17	5.02			
			331.42	N	4.23	4.29			
20	IV	VI	$C_{27}H_{19}N$	C	90.72	91.03	202	—	Dimethoxyethane, orange blades
				H	5.36	5.33			
			357.45	N	3.92	4.18			
21	IV	VII	$C_{29}H_{19}N$	C	91.31	91.19	193	—	Dimethoxyethane, golden needles
				H	5.02	5.25			
			381.47	N	3.67	3.77			
22	IV	VIII	$C_{29}H_{19}N$	C	91.31	91.54	190–191	—	Dimethoxyethane, golden prisms
				H	5.02	4.87			
			381.47	N	3.67	3.66			
23	IV	IX	$C_{33}H_{21}N$	C	91.85	92.11	235–237	—	Dimethoxyethane, golden plates
				H	4.91	5.03			
			431.53	N	3.25	3.26			
24	IV	X	$C_{33}H_{21}N$	C	91.85	91.35	280–281	—	Dimethylformamide, very small red needles
				H	4.91	5.02			
			431.53	N	3.25	3.33			

A cell arrangement essentially the same as that described by Kolthoff (3) was used to obtain all polarograms. The compartment which isolated the aqueous s.c.e. from the solution under examination by a fine porosity disk was so constructed that solution flow always occurred from the main body of the cell into the s.c.e. compartment. In all cases, 50 ml of solution was used to load the cell. These solutions were prepared by weighing a portion (3–7 mg) of the appropriate Schiff base into a dry volumetric flask (50 ml) which contained either n-Pr_4NClO_4 or n-Bu_4NClO_4 (ca. 1.4 g). The flask was then transferred to a dry box and diluted to volume with purified DMF. All subsequent operations with the solution were carried out under pure dry nitrogen. Polarograms were recorded at $T = 25 \pm 1$ °C. The dropping mercury electrode had the following characteristics on open circuit: at $h = 36.5$ cm, $t = 4.91$ s drop^{-1} and $m = 1.64$ mg s^{-1} in 0.1 M KCl saturated with air, giving $m^{2/3} = 1.391$. Duplicate runs demonstrated that the reproducibility of the $E_{1/2}$ values for the first reduction wave was slightly better than 0.01 V. The data recorded from these experiments is recorded in Table II. The I_d values and Nernstian slopes were calculated in the usual manner.

DISCUSSION

All the Schiff bases studied gave two well-defined waves (ω_1 and ω_2) at the initial stages of the reduction, which we assume, following Laitinen and Wawzonek (4), to broadly correspond to the scheme:

$$[1] \quad \mathrm{ArCH{=}NAr'} + \mathrm{e} \rightleftarrows \mathrm{ArCH{=}}\dot{\bar{\mathrm{N}}}\mathrm{Ar'}$$

potential determining (ω_1) reversible

$$[2] \quad \mathrm{Ar}\bar{\mathrm{C}}\mathrm{H{=}}\dot{\mathrm{N}}\mathrm{Ar'} + \mathrm{e} \rightarrow \mathrm{Ar}\bar{\mathrm{C}}\mathrm{H{=}}\bar{\mathrm{N}}\mathrm{Ar'} \ (\omega_2)$$

$$[3] \quad \mathrm{Ar}\bar{\mathrm{C}}\mathrm{H{=}}\bar{\mathrm{N}}\mathrm{Ar'} + 2\mathrm{BH} \rightarrow \mathrm{ArCH_2NHAr} + 2\mathrm{B}^-.$$

In the present communication, we are primarily concerned with the reversibility

TABLE II

Data relating to Schiff bases derived from aniline, 4-aminobiphenyl, 2-aminonaphthalene, and 6-aminochrysene

	Structure			Diffusion current constant			
No.	$ArNH_2$	ArCHO	$-E_{1/2}(\omega_1)$ vs. s.c.e.	ω_{1+2}	ω_1	Nernstian slope (ω_1)	$a_{\text{or}}b_{\text{os}}$
			From aniline				
1	I	V	1.83^9	4.98	3.77	0.065	0.571
2	I	VI	1.61	4.13	3.24	0.069	0.546
3	I	VII	1.69^2	4.82	3.57	0.068	0.507
			1.69^6	4.66	3.45	0.068	
4	I	VIII	1.75	4.94	3.64	0.068	0.550
			1.74	4.67	3.41	0.069	
5	I	IX	1.65	4.11	2.66	0.074	0.505
6	I	X	1.36	4.20	2.19	0.043	0.404
			1.35^4	4.69	2.44	0.045	
			From 4-aminobiphenyl				
7	II	V	1.77^8	4.39	2.59	0.062	0.543
8	II	VI	1.56		2.29	0.049	0.43
9	II	VII	1.65	3.98	2.35	0.062	0.482
10	II	VIII	1.68^4	4.68	2.60	0.057	0.523
11	II	IX	1.61	3.98	2.28	0.058	0.480
12	II	X	1.32^7	3.87	2.01	0.044	0.384
			1.32^7	3.65	1.91	0.045	
			From 2-aminonaphthalene				
13	III	V	1.75^3	4.45	2.18	0.057	0.550
14	III	VI	1.55^8	3.97	2.20	0.049	0.439
			1.55^0	4.19	2.53	—	
15	III	VII	1.62^8	4.30	2.52	0.061	0.488
16	III	VIII	1.67^4	4.55	2.42	0.053	0.529
17	III	IX	1.59^0	4.61	2.61	0.060	0.486
18	III	X	1.32	3.86	1.99	0.044	0.389
			1.31^3	4.16	2.14	—	
			From 6-aminochrysene				
19	IV	V	1.66^0	4.00	2.04	0.056	0.484
20	IV	VI	1.47^8	4.12	2.08	0.048	0.386
21	IV	VII	1.56^0	3.96	2.08	0.049	0.430
22	IV	VIII	1.58^4	3.85	1.98	0.049	0.466
23	IV	IX	1.53^4	3.78	1.94	0.057	0.428
24	IV	X	1.27^2	3.79	1.95	0.041	0.342

of process [1], since departures from reversibility at this stage will reduce the significance of the theoretical considerations appropriate to it. It is now generally recognized that Nernstian slopes obtained from d.c. polarograms are not completely reliable criteria of either the number of electrons transferred at a given stage or whether the stage is reversible. These characteristics of a given reduction step are more definitely diagnosed by a.c. polarographic techniques.[2] However, the I_d values for the first two waves in the case of the Schiff bases are similar in magnitude to those observed by Hoijtink and co-workers (6) in a polarographic study of several hydrocarbons in dimethylformamide. In the latter study, both d.c. and a.c. polarograms were examined and these experiments demonstrated that the reduction steps, analogous to [1] and [2] in the case of the Schiff bases, were essentially reversible. This favorable comparison of the I_d values for the two series of compounds provides some support that the first wave in the Schiff base reductions corresponds to a reversible one-electron transfer. Further confirmation of this was recently obtained in experiments where reoxidation at the first reduction stage for two of these compounds was observed using cyclic voltametric techniques (Table III).

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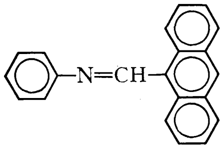
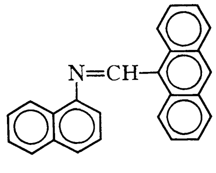
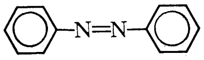
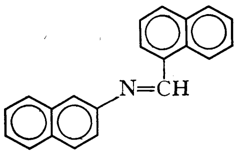
[2] For a very clear account of these problems see Katz, Reinmuth, and Smith (5).

TABLE III

Electron spin resonance and cyclic voltammetric observations

	Electron spin resonance signal*			
	CH_3CN	Dimethoxyethane	DMF	Cyclic voltammetry
	None	—	—	Some reoxidation of $R^{\cdot -}$ just perceptible at 1.5 V s^{-1}, reoxidation still not complete at 9.6 V s^{-1}
	None	None	—	—
† 	Modest signal	—	Somewhat stronger signal	—
	—	—	Stable $R^{\cdot -}$ signal after initial scavenging	Reoxidation of $R^{\cdot -}$ at 5 V min^{-1}, at 12 V s^{-1} oxidation–reduction peaks of ω_1 equal

**in situ* electrolysis at Hg$^{\cdot}$ pool cathode.

†Direct current polarogram gives 2 steps: $I_d(\omega_1) = 2.73$, $I_d(\omega_{1+2}) = 5.04$; Nernstian slope $(\omega_1) = 0.064$.

Because our own data and that of Ono (7) is indicative that Schiff base radical anions are involved in the electrolytic reduction of these substances, we have attempted to test this hypothesis by electrochemical generation of the radical anions, $R^{\cdot -}$, in the cavity of the electron spin resonance (e.s.r.) spectrometer by *in situ* techniques. A stable e.s.r. signal was obtained for only one Schiff base, and this only after a period of apparent scavenging of impurities in the solvent by the generated $R^{\cdot -}$ (Table III). Failure to obtain an e.s.r. signal cannot be considered as conclusive evidence that radical anions are not involved in the reduction. For example, similar experiments with azo compounds indicate that success with this technique is not independent of the structure of the compound under investigation (8). Thus, while d.c. polarograms of azobenzene and 2,2′-azobiphenyl showed very similar characteristics, an e.s.r. signal was only obtained with the former compound (Table III).

Until more complete data utilizing a.c. and e.s.r. techniques become available, the reversibility or "approximate reversibility" (cf. Streitwieser (1, p. 174)) of step [1] will be explicitly assumed.

Application of the H.m.o. theory to the half-wave potentials has necessitated two further assumptions as well as those usually made in this type of study.[3] The first of these concerns the stereochemistry of the Schiff bases, all of which are considered to be in their *trans* forms and planar. Departures from planarity as a consequence of non-bonded interactions between either nitrogen lone pairs and ring bound hydrogens, or extracyclic double-bond bound hydrogens and ring bound hydrogens, are likely to distort the Schiff bases. This apparently contradicts the second stereochemical assumption, but, in view of the more drastic assumptions already made above (see refs. 1 and 9), we feel justified in neglecting this issue completely.

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[3] For details see Hoijtink (9) and Streitwieser (1, p. 175).

The theoretical model for the reduction process envisages the transfer of an electron from the electrode to the lowest vacant molecular orbital of the Schiff base; the second important assumption is concerned with the calculation of this level for each individual structure. It is possible to calculate these levels in the usual manner by setting up the various secular determinants appropriate to each Schiff base, including suitable parameters for the nitrogen heteroatom. Because the Schiff base structures are "large" and lack symmetry, the expansion of each secular determinant and the solution of the resulting secular equations is a formidable task.[4] This has been avoided in the following way. The presence of the heteroatom has been ignored, and the calculations have been made for the corresponding olefin (i.e. ArCH=NAr'≡ArCH=CHAr') using a perturbation method originally employed by Dewar in a theoretical discussion of the K-band spectra of some polycylic aromatic hydrocarbons (10). This rather drastic assumption is justified here because it leads to a simple equation which is extremely useful in practice. The perturbation technique will be presented only in outline, since several excellent accounts of it are available (11–13).

Briefly, the olefin ArCH=CHAr' is considered to be formed from the two arylmethyl radicals $ArCH_2^{\cdot}$ and $Ar'CH_2^{\cdot}$ which unite in the sense:

$$[4] \quad ArCH_2^{\cdot} + Ar'CH_2^{\cdot} \xrightarrow{-2H} ArCH{=}CHAr' \ .$$

The energies of the lowest occupied and highest unoccupied molecular orbitals of the olefin can be calculated very simply in terms of the non-bonding molecular orbital (n.b.m.o.) coefficients at the extracylic carbon atoms of the parent free radicals $ArCH_2^{\cdot}$ (n.b.m.o. coefficient a_{or}) and $Ar'CH_2^{\cdot}$ (n.b.m.o. coefficient b_{os}).

$$[5] \quad E(\text{lowest unoccupied}) = -a_{or}b_{os}\beta$$

$$[6] \quad E(\text{highest occupied}) = a_{or}b_{os}\beta,$$

where β is the carbon–carbon resonance integral of the H.m.o. method and the energy scale corresponds to that where α, the carbon coulomb integral, is taken as zero. The various values of a_{or} or b_{os} for particular arylmethyl radicals are readily calculated by the method of Longuet-Higgins (14). Equation [5] combined with the considerations elaborated elsewhere (1, 9) gives

$$[7] \quad E_{1/2} = -a_{or}b_{os}\beta + C,$$

where C is a constant and $E_{1/2}$ refers to the half-wave potential appropriate to the first wave. A plot of $E_{1/2}$ against $a_{or}b_{os}$ (Fig. 1) gives a reasonably satisfactory correlation when due consideration is given to the extensive approximations made in deriving eq. [7]. The least squares correlation line is

$$[8] \quad E_{1/2} = -a_{or}b_{os}(2.30 \pm 0.10) - (0.51 \pm 0.05),$$

giving a value of $\beta = -2.30$ eV/mole, which lies nicely in the "reduction potential range" of β (1).

The correlation (Fig. 1) does not exhaust the possibilities of eq. [7]. Consider two series of Schiff bases (a) and (b), the (a) series being related to aniline (n.b.m.o. coefficient b_{os}^{a}) and the (b) series being

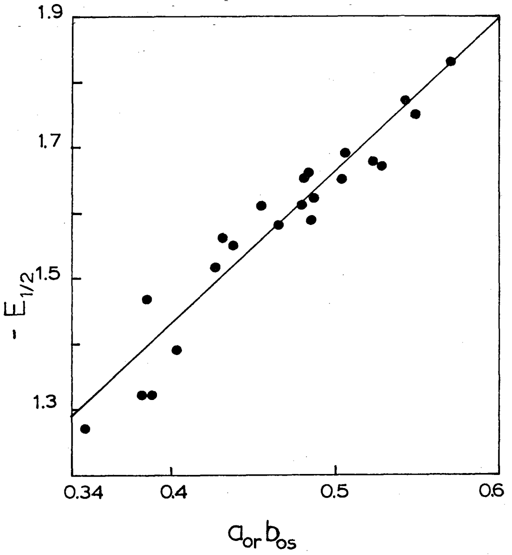

FIG. 1. A correlation between $E_{1/2}(\omega_1)$ for a series of Schiff bases and the $a_{or}b_{os}$ l.c.m.o. parameter.

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[4] At the time this study was undertaken no electronic computer facilities were available to us. This situation has now been remedied and the H.m.o. levels of these compounds will form the subject matter of a subsequent communication.

related to 4-aminobiphenyl (n.b.m.o. coefficient $b^{\mathrm{b}}_{\mathrm{os}}$). Equation [7] applied to series (a) gives

$$[9] \qquad E_{1/2}(\mathrm{a}) = -a_{\mathrm{or}}b^{\mathrm{a}}_{\mathrm{os}}\beta + C$$

and applied to series (b) gives

$$[10] \qquad E_{1/2}(\mathrm{b}) = -a_{\mathrm{or}}b^{\mathrm{b}}_{\mathrm{os}}\beta + C.$$

Equations [9] and [10] may be rearranged to give

$$[11] \qquad \frac{E_{1/2}(\mathrm{a}) - C}{b^{\mathrm{a}}_{\mathrm{os}}} = -a_{\mathrm{or}}\beta$$

$$[12] \qquad \frac{E_{1/2}(\mathrm{b}) - C}{b^{\mathrm{b}}_{\mathrm{os}}} = -a_{\mathrm{or}}\beta.$$

Combining eqs. [11] and [12] by elimination of the term $-a_{\mathrm{or}}\,\beta$ gives

$$[13] \qquad \frac{E_{1/2}(\mathrm{a}) - C}{b^{\mathrm{a}}_{\mathrm{os}}} = \frac{E_{1/2}(\mathrm{b}) - C}{b^{\mathrm{b}}_{\mathrm{os}}}$$

or

$$[14] \quad E_{1/2}(\mathrm{a}) = \frac{b^{\mathrm{a}}_{\mathrm{os}}}{b^{\mathrm{b}}_{\mathrm{os}}} E_{1/2}(\mathrm{b}) + C(1 - b^{\mathrm{a}}_{\mathrm{os}}/b^{\mathrm{b}}_{\mathrm{os}}).$$

Since the ratio $b^{\mathrm{a}}_{\mathrm{os}}/b^{\mathrm{b}}_{\mathrm{os}}$ is a constant, eq. [14] may be written in the form

$$[15] \qquad E_{1/2}(\mathrm{a}) = AE_{1/2}(\mathrm{b}) + B,$$

where A and B are constants.

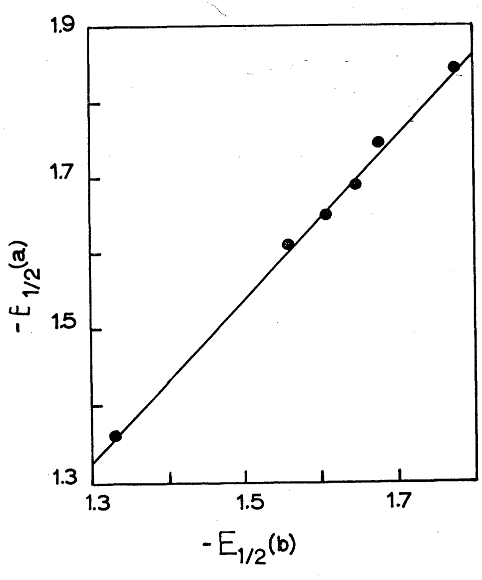

FIG. 2. A correlation of $E_{1/2}(\omega_1)$ for Schiff bases derived from aniline versus $E_{1/2}(\omega_1)$ for Schiff bases derived from 4-aminobiphenyl.

One of the correlations predicted by eq. [15] is displayed in Fig. 2 for the amine pair aniline – 4-aminobiphenyl, and the amine pairs aniline – 2-aminonaphthalene and aniline – 6-aminochrysene give equally good correlations. The excellence of these correlations partially justifies the assumptions made in deriving eq. [7] and suggests that a more refined m.o. treatment in which the presence of the nitrogen atoms in the Schiff bases are specifically included would yield expressions similar in form to eqs. [7] and [15].

Since the $E_{1/2}$ values are essentially free energies, eq. [15] is a linear free energy relationship (15–17). Consequently, it should be possible to cast the reduction potential data in a σ–ρ form.[5] For this purpose it is necessary to define a "standard reduction" and a "standard reduction series". For the former, it is convenient to choose the benzanil reduction

$$[16] \quad \mathrm{PhCH{=}NPh} + \mathrm{e} \rightleftharpoons \mathrm{PhCH{=}\dot{N}Ph} \quad E^0_{1/2}.$$

The "standard reduction series" is then developed by changes in the structure of the aldehyde fragment of the Schiff base, i.e. by means of the reduction

$$[17] \quad \mathrm{ArCH{=}NPh} + \mathrm{e} \rightleftharpoons \mathrm{ArCH{=}\dot{N}Ph} \quad E_{1/2},$$

where the aryl groups Ar- are those appropriate to the aldehydes VI to X. The sigma values for these reductions (denoted by σ_{r} to differentiate them from the Hammett σ constants) are then defined as

$$[18] \qquad \sigma_{\mathrm{r}} = E_{1/2} - E^0_{1/2}.$$

Values of σ_{r} calculated according to eq. [18] are given in Table IV. These can be applied to a related reduction series by plotting the σ_{r} values against the $E_{1/2}$ values for the Schiff bases derived from 4-aminobiphenyl, 2-aminonaphthalene, and 6-aminochrysene. Two of these plots are illustrated in Fig. 3 and, as might have been anticipated from the correlation in Fig. 2, excellent linear relationships are obtained. Finally, if we combine eqs. [7] and [18] we obtain

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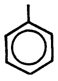
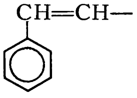
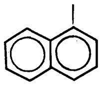
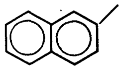
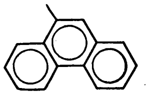
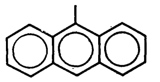
[5] For a similar treatment of some solvolytic rate data see ref. 1, Chap. 12, p. 372.

TABLE IV

Rate and half-wave potential data for various aromatic derivatives including σ_r values

Structure, Ar	σ_r	$-E_{1/2}$(17), ArCHO	Log k_{25}*	Log k_{50}† (ref. 21)
	0	1.553	−3.29 (19)	−2.17
	0.229	1.296	−2.48 (20)	—
	0.145	1.437	−2.65 (19)	−1.16
	0.094	1.466	−2.87 (19)	−1.30
	0.189	1.410	−2.58 (19)	−0.890
	0.482	1.168	−1.42 (19)	—

*S_N2 I^- attack on $ArCH_2Cl$.
†H/D exchange of α,α,α-d_3-methylarenes.

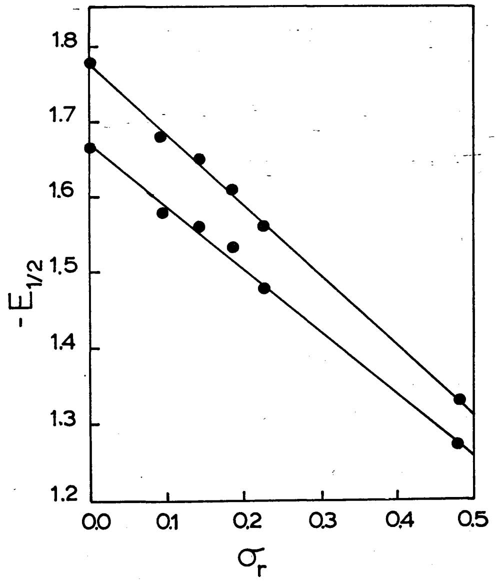


FIG. 3. A correlation of $E_{1/2}(\omega_1)$ values versus σ_r: (upper curve) 4-aminobiphenyl series, (lower curve) 6-aminochrysene series.

$$\sigma_r = b^0_{os}(a^0_{or} - a_{or})\beta, \quad [19]$$

where b^0_{os} is the n.b.m.o. coefficient of the standard amino fragment and a^0_{or} is the n.b.m.o. coefficient of the standard aldehyde fragment. The coefficients a_{or} (which is the variable term in eq. [19]) are those appropriate to the aldehydes which made up the standard reduction series. A new reaction series is generated when the standard amine is replaced by a new amine of n.b.m.o. coefficient b'_{os}, while the variation of the aldehyde structures remains the same as that in the standard reduction series. For this new series, which we denote by primed $E_{1/2}$'s, we obtain from eq. [7]

$$E'_{1/2} - E^{0\prime}_{1/2} = b_{os}(a^0_{or} - a_{or})\beta, \quad [20]$$

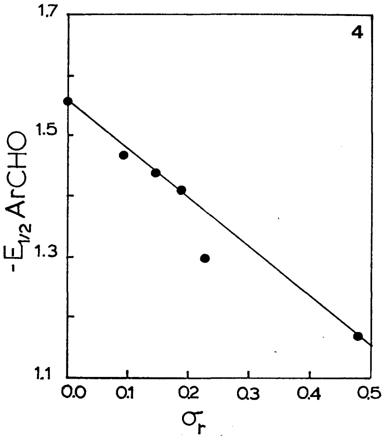
which on eliminating the term $(a^0_{or} - a_{or})\beta$ by means of eq. [19] gives

$$E'_{1/2} - E^{0\prime}_{1/2} = \frac{b'_{os}}{b^0_{os}}\sigma_r. \quad [21]$$

If we now write the ratio b'_{0s}/b^0_{0s} as ρ_r, since this is a constant by definition, eq. [21] takes on the Hammett form, i.e.

$$[22] \qquad E'_{1/2} - E^{0\prime}_{1/2} = \rho_r\sigma_r.$$

Clearly, since the parameter ρ_r is related to the n.b.m.o. coefficients of the amines which define the standard and new reaction series, it should be possible to calculate the magnitude of ρ_r theoretically and hence predict the slopes of the $E_{1/2}$ versus σ_r correlations. However, within the confines of the present data (only four amine structures) we do not propose to pursue this matter further at the present time.



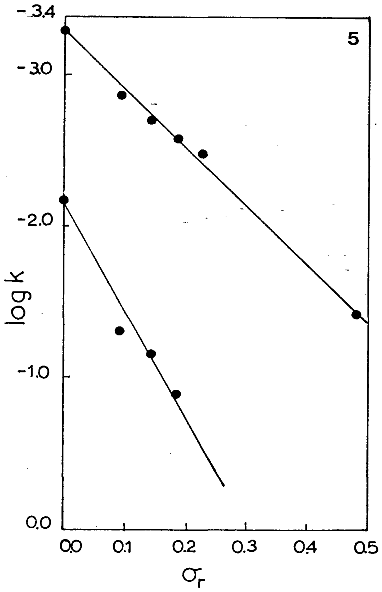


FIG. 4. A correlation between σ_r and the reduction potentials for a series of arylaldehydes.

FIG. 5. A correlation between σ_r and rate constants: (upper curve) S_N2 displacement reactions of arylmethylchlorides and iodide ion in acetone, (lower curve) lithium cyclohexamide catalyzed D—H exchange of d_3-methylarenes.

Of considerably greater interest is the correlation of the σ_r parameter with other reactivity data available from the literature and recorded in Table IV. In Fig. 4 we have plotted the σ_r values against the reduction potentials of the related aldehydes (18) and, apart from cinnamaldehyde, an excellent correlation is obtained. Similarly, in Fig. 5 we have plotted the σ_r values against (*a*) the logarithms of the rate constants for S_N2 iodide ion replacement reactions of the structurally related arylmethyl chlorides (19, 20) and (*b*) the logarithms of the rate constants for the hydrogen–deuterium exchange reactions of the structurally related α,α,α-d_3-methylarenes catalyzed by lithium cyclohexamide in cyclohexylamine (21). The excellence of these correlations is indicative that the σ_r values are structure-reactivity indices of considerable utility.

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