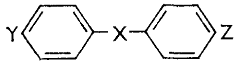
41. *The Transmission of Electronic Effects in Substituted Diphenyl Sulphides, Diphenyl Oxides, and Diphenylamines.*

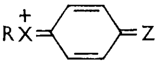
By K. Boček, A. Mangini, and R. Zahradník.

The influence of nitro- and keto-substituents on the polarographic half-wave potentials and infrared spectra of diphenyl sulphides diphenyl oxides, and diphenylamines has been investigated. Interaction between these functional groups and donor substituents (OMe, NH_2, NMe_2) in the second benzene nucleus is very limited: it is concluded that in the ground state electronic effects are not appreciably transmitted through S, O, or NH bridges.

This paper deals with the polarographic reduction and infrared spectral properties of the group Z (NO_2 or Ac) in compounds (I), where X = O, S, or NH and Y = H, OMe, NH_2, or NMe_2, in an attempt to assess the influence of Y on the local electron distribution of Z in the ground state of the molecule, and thus on the ability of X to conduct the perturbation *via* the two benzene nuclei.

(I)





(II)

Compounds (I) are not planar,[1] the two π-systems C_6H_4Y and C_6H_4Z being twisted in respect of the direction of the doubly occupied valency orbital of X which is a $2p_z$, $3p_z$, or a $2s2p$ hybrid for X = O, S, or NH, respectively. In the ground state of the molecules an atom X will interact with the electron-acceptor group Z inductively and by participation of structures such as (II), so that, if second-order effects are neglected, any influence of Y on Z will be due to modification of the electronic character of the bridging group X.

When X = O or NH, the perturbation is expected to be inductive, since oxygen and nitrogen do not possess readily available empty orbitals which can accept a fraction of the charge distribution from the π-system C_6H_4Y. When X = S, empty orbitals, although energetically unfavourable and diffuse, exist on the valency shell, namely, $3d$-orbitals. Many authors have claimed their effectiveness in an acceptor mechanism by sulphur: if this is valid, we may expect marked differences in the properties of molecules (I) (and thus of the group Z) between cases when X = O or NH and cases when X = S.

Experimental

Polarographic measurements were carried out with an apparatus of " Heyrovský " type V 301 (1952). A galvanometer with a sensitivity $2{\cdot}3 \times 10^{-9}$ amp./mm. was used. The measurements were performed in the Kalousek cell [2] with a normal calomel electrode. Half-wave potentials given here refer to this electrode. The drop time of the capillary used was 2·6 sec. (length 8·5 cm.) at a flow rate of 3·75 mg./sec.

The polarographic waves pertaining to reduction of the nitro-group were recorded for 0·001M-ethanolic solutions (1·00 ml.) of nitro-compounds in a buffer solution (9·00 ml.) prepared from 0·2M-citric acid and 0·2M-disodium hydrogen phosphate in 50% (v/v) methanol. For the acetyl derivatives the polarographic waves were recorded for 0·001M-ethanolic solutions (2·00 ml.) with the same buffer solution (8·00 ml.).

The potential gradient was adjusted by means of the normal Weston cell; the values of the half-wave potentials were checked with the waves of Tl^+ ions [$E_{1/2}$ (Tl^+) = −0·50 v]. The average values of the half-wave potentials are collected in Table 1.

Infrared spectra were recorded on a double-beam spectrophotometer of Zeiss (Jena) model UR-10, with a sodium chloride prism (resolving power 6 cm.$^{-1}$) for 0·1M-chloroform solutions in cells of 0·1 mm. thickness. The estimated error of wave numbers is ±1 cm.$^{-1}$, and the root

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[1] Toussaint, *Bull. Soc. chim. belges*, 1948, **54**, 319.

[2] Heyrovsky and Kalousek, *Coll. Czech. Chem. Comm.*, 1939, **11**, 464.

TABLE 1.

Polarographic half-wave potentials $E_{1/2}$ (v; ±0·01 v) of nitro- and acetyl groups in compounds (I).

X	Y	pH			pH		
		2·15	5·9	9·2	2·15	6·0	9·2
			Nitro-groups.			Acetyl groups.	
S	NMe_2	−0·28	−0·49	−0·72	−1·13	−1·36	−1·58
S	NH_2	−0·26	−0·47	−0·72	−1·09	−1·38	−1·58
S	OMe	−0·28	−0·48	−0·73	−1·08	−1·40	−1·58
S	H	−0·27	−0·48	−0·74	−1·08	−1·37	−1·56
O	NMe_2	−0·30	−0·54	−0·75	—	—	—
O	NH_2	−0·31	−0·55	−0·76	−1·17 *	−1·47	−1·71
O	OMe	—	—	—	−1·20 *	−1·47	−1·71
O	H	−0·32	−0·56	−0·78	−1·16 *	−1·47	−1·71
NH	NMe_2	−0·31 †	−0·61	−0·81	—	—	—
NH	NH_2	−0·29 †	−0·60	−0·82	—	—	—
NH	OMe	−0·36	−0·61	−0·85	−1·17 *†	−1·54	−1·77
NH	H	−0·35	−0·60	−0·85	−1·15 *†	−1·58	−1·78

* Depolarisation of the hydrogen ions interferes with the waves of the keto-group. † Protonation takes place.

TABLE 2.

Infrared data for the nitro-group in compounds (I).*

Y	X	ν_s (cm.$^{-1}$)	ν_{as} (cm.$^{-1}$)	ε_s † (10^3 l. mole^{-1} cm.$^{-1}$)	ε_{as} † (10^3 l. mole^{-1} cm.$^{-1}$)	q
NMe_2	S	1345	1522	1·51	0·877	$1{\cdot}7_2$
NH_2	S	1345	1521	1·49	0·702	$2{\cdot}1_2$
OMe	S	1346	1522	1·30	0·614	$2{\cdot}1_1$
H	S	1346	1526	1·06	0·445	$2{\cdot}3_8$
NMe_2	O	1351	1524	1·32	1·250	$1{\cdot}0_6$
NH_2	O	1351·5	1520	1·26	0·948	$1{\cdot}3_3$
H	O	1353	1528	1·02	0·550	$1{\cdot}8_5$

* The values of ε, $\Delta\nu_{1/2}$, and B (Tables 2 and 3) are not corrected for the final slit width. In the present connexion it is unnecessary to do so. † $\varepsilon = (1/cd) \log_{10} (I_0/I)$ (l. mole^{-1} cm.$^{-1}$).

TABLE 3.

Infrared results for keto-group in compounds (I).

Y	X	ν(C = O) (cm.$^{-1}$)	$\varepsilon_{max.}$ (10^2 l. mole^{-1} cm.$^{-1}$)	$\Delta\nu_{1/2}$ (cm.$^{-1}$)	$B = \varepsilon\Delta\varepsilon_{1/2}$ (10^4 l. mole^{-1} cm.$^{-2}$)
NMe_2	S	1686	4·90	20·0	0·98
NH_2	S	1689	4·79	19·0	0·91
OMe	S	1688	4·91	17·5	0·86
H	S	1690	4·79	17·0	$0{\cdot}81_5$
NH_2	O	1689	4·35	20	0·87
OMe	O	1689	4·53	19	0·86
H	O	1689	4·38	18·5	0·81

TABLE 4.

Infrared results for the nitro-group in *para*-substituted nitrobenzenes.

Subst.	NMe_2	NH_2	SMe	OMe	H
ν_s (cm.$^{-1}$)	1326	1337	1342	1349	1350
ν_{as} (cm.$^{-1}$)	1501	1511	1522	1523	1530
q	4·70	2·12	2·11	1·40	0·99

mean square error of the quantity q is ±10%. Frequencies and intensities were measured for the symmetrical and antisymmetrical stretching vibrations of the nitro-group (Table 2), and for the stretching vibrations of the keto-group of the acetyl derivatives where X = S or O (Table 3). Analogous measurements for some *para*-substituted nitrobenzenes are collected in Table 4.

DISCUSSION

Polarographic Results.—From Table 1 it appears that the $E_{1/2}$ values of reduction for nitro- and keto-groups are not affected by the nature of the other substituent Y for any of the compounds (I) where X = O, NH, or S, in agreement with findings by Jaffé *et al.*;[4] this indicates that the interaction between the functional group Z and the donor substituent Y is not appreciable, being of the same order of magnitude as the experimental error. In fact the Hammett ρ-values for polarographic reduction of substituted nitrobenzenes and acetophenones[5] are 0·23 (average) and 0·35, respectively, so that the transition from unsubstituted to *p*-amino-derivatives [σ_p (NH_2) = 0·66 (ref. 6)] is connected with a change in $E_{1/2}$ of about 0·15 and 0·23 v, respectively. (The σ-constant of the NMe_2 group is uncertain.[7])

Introduction of a substituent with a larger negative value of the σ-constant is, of course, connected with the shift to larger negative values of the half-wave potential. The direction of the very small systematic shift found in several cases (cf. Table 1) is the opposite. It may, therefore, be concluded that the ρ-constant of the system under study is approximately zero.

Infrared Spectra.—The stretching frequencies of group Z are not very sensitive to the influence of the substituent Y (see Tables 2 and 3). This also supports the hypothesis of a very limited interaction through the bridge X, in agreement with the conclusions from electronic spectra.[8]

The values[9] of the parameter *q* lead to the same result. This quantity is defined as $\varepsilon_s/\varepsilon_{as}$ where $\varepsilon_{s/as}$ is the maximum molar extinction coefficient of the symmetrical/antisymmetrical stretching vibration of a group. In principle, the ratio of the integrated absorption intensities would have more theoretical meaning, but when, as here, the half-width is roughly constant the ratio of the extinctions is adequate. The quantity *q* can be taken as a measure of the electronic interaction between the functional group characterized by the above-mentioned vibrations and the substituent.[9] The changes in *q* caused when Y is changed from H to NMe_2 are much smaller, especially when X = S, than those for *para*-substituted nitrobenzenes (see Table 4). For X = O the trend of the *q*-values is more pronounced (Table 2).

The sign of the Hammett constants (in the dependence of *q* on σ) in the nitro-compounds (I) is the reverse of that in *para*-substituted nitrobenzenes; and the cause of this, already noted for the polarographic reductions, is not clear. Another discrepancy, the position of SMe in the perturbation order of Table 4, may be explained, at least partly, as due to the non-constancy of the band half-width.

The absorptivities of the carbonyl stretching-vibration bands remain nearly constant for all substituents here studied: this is, however, not very significant because the ρ-constant is very small or zero in substituted acetophenones as far as the infrared absorptivities are concerned.[9]

Conclusions.—The following conclusions are drawn: (i) In connexion with the ability of the bridging group to relay an electronic effect it has been found that sulphur behaves analogously to the other first-row elements, oxygen and nitrogen. This means that 3*d*-orbital participation in the ground state of the molecules here studied is not effective (within experimental error). (ii) As could have been anticipated for energetic reasons, the

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[3] Perkampus and Köhler, *Z. Elektrochem.*, 1957, **61**, 836.

[4] Jaffé and Otsuji, Report Petroleum Research Fund, 1960, 301-A, p. 60.

[5] Zuman, *Chem. listy*, 1954, **48**, 94.

[6] Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[7] van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

[8] Cf. ref. 35 cited by Mangini, *Boll. sci. Fac. Chim. ind. Bologna*, 1960, **18**, 191.

[9] Zahradník and Boček, *Coll. Czech. Chem. Comm.*, 1961, **26**, 1733; Boček and Zahradník, *Spectrochim. Acta*, 1962, **18**, 564.

[10] Thompson, Needham, and Jameson, *Spectrochim. Acta*, 1957, **9**, 208.

long-distance perturbation between groups Y and Z is very small. The situation is not yet completely clear in connexion with the *q*-values, since the donor power of the substituent Y affects the *q*-values in a sense contrary to expectation.

Istituto di Chimica Industriale, University of Bologna, Italy.
Institute of Industrial Hygiene and Occupational Diseases,
Prague, Czechoslovakia.
[Present address (K. B., R. Z.): Institute of Physical Chemistry, Academy of Science,
Máchova, Prague, 2.]

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