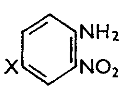
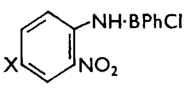
725. *Some Highly Coloured* o-*Nitroanilinoboron Halides.*

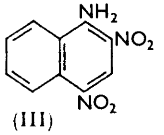
By J. C. LOCKHART.

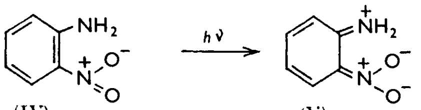
Substituted *o*-nitroanilinoboron halides are reported. Solvent and substituent effects on the longest-wavelength visible absorption band of *o*-nitroanilines and their boron derivatives are discussed.

REACTION of *o*-nitroanilines (I) with phenylboron dichloride formed the substitution products (II). The presence of the *o*-nitro-group has a marked effect on the spectrum of the substitution product. For instance, *o*-nitroanilinophenylboron chloride (II; X = H) is purple.[1] Formation of the anilinoboron compounds is effectively instantaneous at room temperature in inert solvents. Visible and accessible ultraviolet absorption spectra of these compounds, the parent nitro-amines, and related compounds have now been examined.[2,3]


(I)


(II)


(III)


(IV) (V)

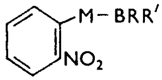

(VI)

TABLE 1.

Spectra of *o*-nitroaniline (I; X = H) and its boron derivatives (II; X = H) in various solvents.

	Compound (I)		Compound (II)	
Solvent	$\lambda_{\text{max.}}$ (mμ)	ε	$\lambda_{\text{max.}}$ (mμ)	ε
Hexane *	374	4760		
Cyclohexane †	376	4930	504 ‡	
CCl_4 *	383	5000	511— 512 ‡	
Butyl bromide *	388	5020		
Ether *	388	5400	514	4150
CH_2Cl_2 *	395	5000		
Benzene †	392	5020	516	2700
Chlorobenzene *	391	5020	518	2680

* Containing 4% of benzene. † Pure solvent. ‡ Very insoluble.

TABLE 2.

Spectra in aqueous solutions of *o*-nitro-amines (I) and (III) and their conjugate acids.

X in (I)	Solvent	$\lambda_{\text{max.}}$ (mμ)	ε	pK_a
H	pH 6	409	4500	$-0{\cdot}25$[2]
Me	,,	284; 425	5230; 4250	$+0{\cdot}13$
cation	12% H_2SO_4	262	6500	
MeO	pH 6	284; 446	4850; 4600	$+0{\cdot}43$
cation	12% H_2SO_4	270; 328	1900; 4900	
Cl	pH 2	423	4400	$-0{\cdot}97$[2]
NO_2	45% $HClO_4$	348; 400	12,300; 6500	$-4{\cdot}36$[3]
Compound (III)	,,	395; 445	10,500; 5300	$-6{\cdot}37$[3]

Solvent Effects.—Tables 1 and 2 illustrate the effect of solvent on the absorption spectra of certain *o*-nitroanilines and *o*-nitroanilinoboron chloride (II; X = H). Increase in

---

[1] Lockhart, *Chem. and Ind.*, 1961, 2006.
[2] Long and Paul, *Chem. Rev.*, 1957, **57**, 1.
[3] Bonner and Lockhart, *J.*, 1957, 2840.

solvent polarity causes a red shift, indicating an excited state more polar than the ground state. The visible band in the *o*-nitroanilines disappears in the *o*-nitroanilinium ion (Table 2); thus the associated transition involves the non-bonding electrons of the amino-group. Proximity of the negatively charged nitro-oxygen can stabilise positive charge in form (V) more than is possible in *p*-nitroaniline where such interaction would be intermolecular.

Effect of Ring Substituents.—These effects are recorded in Tables 2 and 3. A plot of

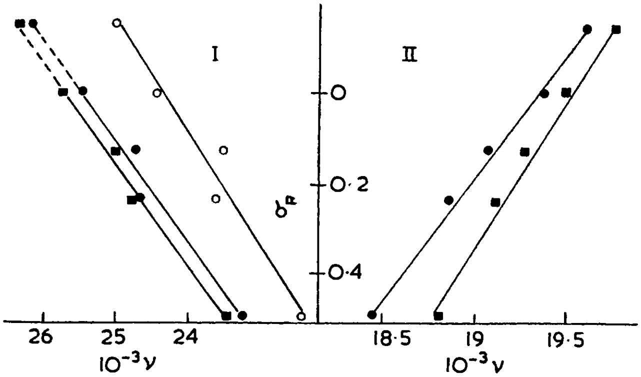


FIG. 1. Correlation of the frequency of the lowest-energy absorption band with σ_R values of (I) *o*-nitroanilines and (II) *o*-nitroanilinoboron dichlorides.

■ In ether; ● in benzene; ○ in water.

ν, the frequency of the lowest-energy band (proportional to the energy of the transition involved), against σ_R, a set of substituent constants said to be concerned with resonance effects only,[4] is a straight line for both the amines (I) and the anilinoborons (II) (Fig. 1).

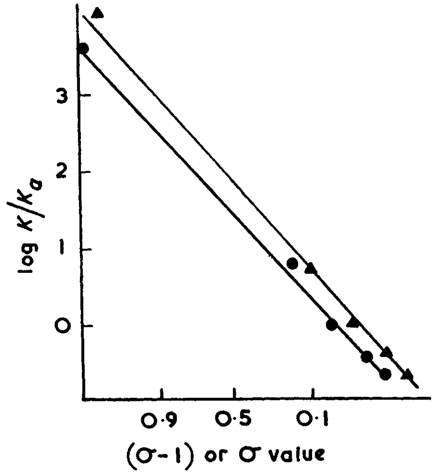


FIG. 2. Correlation of σ-values with pK_a for (●) aniline and (▲) *o*-nitroaniline derivatives (slopes 2·72 and 2·91, respectively).

The simple σ-constants [5] said to represent steric, inductive, and resonance effects cannot be correlated with our results, nor can pK_a values for the *o*-nitroanilines themselves. The pK_a values of the *o*-nitroanilines can be correlated with σ-values and have approximately

---

[4] Taft, in Newman's " Steric Effects in Organic Chemistry," John Wiley and Sons Inc., New York, 1956, p. 595.

[5] McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420.

the same ρ-values as the parent amines[6] (Fig. 2). The resonance effect must be preponderant for the transition associated with the visible absorption band.

The transition causing the purple colour in the anilinoborons presumably involves boron and the nitro-group. The colours are observed only in systems such as (VI), in which boron is linked to the aromatic ring through nitrogen[1] or oxygen.[7] Boron linked directly *ortho* to a nitrobenzene ring does not greatly modify the nitrobenzene spectrum. *o*-Nitrophenylboronic acid[8] is pale yellow ($\lambda_{max.}$ 273 mμ in water).

The effects of other substituents in a compound of type (VI) are as follows. In general, increase in electron density at M (which increases back co-ordination from M to boron) appears to decrease the transition energy; electron-donating substituents *para* to the amino-group decrease the transition energy, but in the less basic molecule (VI; M = NPh) the transition energy is increased (see Table 3).

TABLE 3.

Effect of substituents on the spectra of *o*-nitroanilines and their boron derivatives (cf. II).

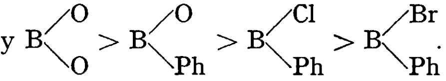
	Amine				Aminoboron (cf. II)			
	in ether		in benzene		in ether		in benzene	
X	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε
o-*Nitroanilines* (I)								
NO_2	380 *	5680	382 *	4950	506	3870	510	3600
H	388	5400	392	5020	513	4150	516	2700
Me	399·5	5150	404	4880	519	3860	524	2800
Cl	404	5290	408	5000	523	4150	530	2900
MeO	426	5540	430	5380	532	4200	542	3200
Related compounds								
o-$NO_2{\cdot}C_6H_4{\cdot}NHPh$	416	6700	422	6500	—	—	—	—
1,2,4-$NO_2{\cdot}C_6H_3(NH_2)_2$	371	9700	—	—	432	7300	—	—
4,2,1-$(NO_2)_2C_6H_5{\cdot}NH_2$	372 *	—	375 *	—	—	—	487	—

* Resolved value.

TABLE 4.

Absorption peaks for compounds (VI; M = NH).

R	$\left.\begin{matrix}-O\\-O\end{matrix}\right>[CH_2]_2$	Ph	Ph	Ph
R′		Br	$-O{\cdot}[CH_2]_2{\cdot}Cl$	Cl
$\lambda_{max.}$ (mμ)	535	528	520	516

For substituents on boron the order of back-co-ordination[9] from R and R′ in (VI; M = NH) is probably  $B\left<\begin{matrix}O\\O\end{matrix}\right. > B\left<\begin{matrix}O\\Ph\end{matrix}\right. > B\left<\begin{matrix}Cl\\Ph\end{matrix}\right. > B\left<\begin{matrix}Br\\Ph\end{matrix}\right.$. However, no simple relationship with the transition energy is apparent in Table 4. It is reasonable to assume donation from the amino-group to boron in the excited state. In such a situation, the more saturated the boron the higher would be the transition energy, and the more basic the nitrogen the lower the transition energy. The evidence is not entirely in favour of this and a direct interpretation is not obvious at this stage.

An example of boron as donor in the excited state occurs in the coloured bispyridinodecaborane.[10] Here the boron donates directly to pyridine. Evidence for beryllium as a donor in bipyridylberyllium complexes has also been obtained.[11]

---

[6] Taft and Lewis, *J. Amer. Chem. Soc.*, 1959, **81**, 5343.

[7] Colclough, Gerrard, and Lappert, *J.*, 1956, 3006.

[8] Seaman and Johnson, *J. Amer. Chem. Soc.*, 1931, **53**, 711.

[9] Skinner and Smith, *J.*, 1954, 3930; Cotton and Leto, *J. Chem. Phys.*, 1959, **30**, 993.

[10] Graybill and Hawthorne, *J. Amer. Chem. Soc.*, 1961, **83**, 2673.

[11] Coates and Green, *Proc. Chem. Soc.*, 1961, 376.

EXPERIMENTAL

o-*Nitroanilinophenylboron Chloride.*—To *o*-nitroaniline (1 mol.) in ether was added phenylboron dichloride (excess). The purple precipitate was filtered from the vivid purple solution. The crystals decomposed almost instantly in moist air or in water, giving the amine (or amine hydrochloride) and phenylboronic acid. Their reactivity and insolubility rendered purification difficult. The products from dinitroaniline and 2,4-dinitro-1-naphthylamine could not be obtained pure. However, the chloro-, methyl, and methoxy-derivatives were made by this method, as follows. o-*Nitroanilinophenylboron chloride* (Found: B, 4·1; Cl, 13·9; amine, 52·7. $C_{12}H_{10}BClN_2O_2$ requires B, 4·15; Cl, 13·6; 52·2%); 4-*methyl*- (Found: B, 4·0; Cl, 12·7; amine, 54·9. $C_{13}H_{12}BClN_2O_2$ requires B, 3·9; Cl, 12·9; amine 55·2%), 4-*methoxy*- (Found: B, 3·4; Cl, 11·7; amine, 59·4. $C_{13}H_{12}BClN_2O_3$ requires B, 3·7; Cl, 12·0; amine, 57·5%), and 4-*chloro-2-nitroanilinophenylboron chloride* (Found: B, 3·5; easily hydrolysed Cl, 11·8; amine, 56·0. $C_{12}H_9BCl_2N_2O_2$ requires B, 3·7; easily hydrolysed Cl, 12·0; amine 57·9%). Amine was estimated spectrophotometrically in water and boron and chlorine by titration (pH-meter).

Spectra.—These were measured in a Unicam S.P. 500 spectrophotometer. The purple compounds were made *in situ* by addition of an excess of boron halide to the nitro-amine. No further reaction took place, with the nitro-amines involved.

pK_a *Values.*—These were estimated spectrophotometrically, H_0 values from Long and Paul's review being used.

The author is most grateful for an I.C.I. Fellowship of the University of London, and thanks Dr. D. Peters for useful discussion.

ROYAL HOLLOWAY COLLEGE,
ENGLEFIELD GREEN, SURREY.

[*Received, February 8th,* 1962.]