



Fig. 2. Visible spectrum of nitrobenzene free radical anion in solution of 0.2 N sodium nitrate in dimethylformamide. Spectrum was made for concentrations of the free radical anion of about 1.3×10^{-4} M and for a cell length of 35 mm

radical anion. By combining this with measurements of extinction for different wave-lengths caused by the presence of the free radical anion, the extinction coefficients of the whole spectrum were calculated.

The visible spectrum of nitrobenzene free radical anion exhibits two distinct maxima: the first is at 435 m μ region and the second at 465 m μ (Fig. 2).

The method applied by us for simultaneous measurements of the optical properties and oxidation current of the nitrobenzene free radical anion can be used for determining the extinction coefficients and spectra of different free radical anions which are stable, or which only slowly decay with time. This method also enables the measurement of the kinetics of the decay of radical anions to be made.

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Electron-donating Properties of Central Sympathetic Suppressants

ELECTRON-TRANSFER reactions between organic substances have often been implicated in various biological processes¹⁻³. Recently, Karreman, Isenberg and Szent-Györgi⁴ have suggested that certain central sympathetic suppressants act by donating electrons on the inside of the electric double layer of the central nervous system. A consequence of this hypothesis would be that pharmacologically active substances should possess relatively low ionization potentials.

Although it has been inferred both from molecular orbital calculations⁴⁻⁶ and charge-transfer spectra⁷ that these substances should be good donors, as yet there have been no reports of ionization potentials of suppressants. Though the direct measurement of ionization potential is quite difficult, it is nevertheless possible to derive values of this quantity from photoelectric measurements on the solid.

The photoelectric threshold, I_C , of a molecular crystal has been shown⁸ to be related simply to the molecular ionization potential, I_G , by:

$$I_C = I_G + P \quad (1)$$

where P is the polarization energy of the crystal. P can be calculated for crystals of known structure.

We have measured I_C for several central sympathetic suppressants and threshold energies are given in Table 1.

Table 1. I_C AND I_G FOR SOME PHARMACOLOGICALLY ACTIVE SUBSTANCES

	I_C (eV)	I_G (eV)
Phenothiazine*	5.14 ± 0.05	6.7
Promazine	5.16 ± 0.05	6.8
Promazine hydrochloride	5.46 ± 0.05	7.1
Chlorpromazine	5.08 ± 0.05	6.7
Chlorpromazine hydrochloride	5.22 ± 0.05	6.8
Trifluoperazine dihydrochloride	5.68 ± 0.10	7.3
Prochlorperazine	$5.45 \pm 0.10^\dagger$	7.1
Reserpine	5.40 ± 0.05	7.0

* Inactive pharmacologically.
† As viscous oil.

I_G is estimated from equation (1) by assuming an average value for P of 1.6 eV (ref. 8). We expect the error in P to be no greater than 0.3 eV.

The measurements indicate that these substances have striking electron-donating properties. Chlorpromazine is an even better donor than the readily oxidizable naphthalene for which $I_C = 5.25$ eV (ref. 9) and $I_G = 6.88$ eV (ref. 10). Low values of I_C for phenothiazine derivatives are seen to be associated with the parent nucleus.

Though it is appreciated that alternative mechanisms of suppression of the central nervous functions are feasible, the present work is consistent with the electron-transfer theory. It must be emphasized, however, that the possession of a low ionization potential does not in itself render a substance pharmacologically active. Phenothiazine, for example, is not a central sympathetic suppressant.

Since such biochemically important molecules as the chlorophylls and β -carotene also have low values of I_C (ref. 11) it is still possible to maintain that electron-transfer reactions may be of importance in many biological processes.

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Photoconductivity of Manganous Phthalocyanine

We have investigated the dark- and photo-conductivity of single crystals of metal-free and some transition metal phthalocyanines. Some of our results for metal-free, zinc, copper, nickel and cobalt phthalocyanines have been published elsewhere¹. Meanwhile we have extended our investigations to include ferrous and manganous phthalocyanines. Here we wish to report briefly that we have found manganous phthalocyanine to differ in its behaviour from the other members of the series in a striking manner. The measurements were made on the needle-shaped crystals using two electrodes. No guard ring was used, and the arrangement is therefore equivalent to a surface conductivity cell.

First, we find the dark resistivity of the manganous compound is much lower than that of the other phthalocyanines. The dark resistivities are presented in Table 1, from which it can be seen that while manganous phthalocyanine has a specific resistivity as low as 10^6 ohms/c.c.,