ELECTRON TRANSFER AND HEAVY ATOM PERTURBATION IN SYSTEMS OF HALOGENATED TYROSINES AND MENADIONE[1]

Sir:

Saturated aqueous solutions of menadione and dissociated orthoiodinated phenols produce instantaneously a pinkish color which is reversibly weakened by warming. Spectroscopic examination shows a new, wide band with a maximum near 520 mμ, whose short wave length side is overlapped by the vitamin absorption. Despite the lability of the system one seems to find that the band has a trace of fine structure. This point is confirmed by adding the menadione in acetone solution (Fig. 1). A clear example for purely aqueous solutions is furnished by *p*-benzoquinone and 3,5-diiodo-4-hydroxybenzoic acid.

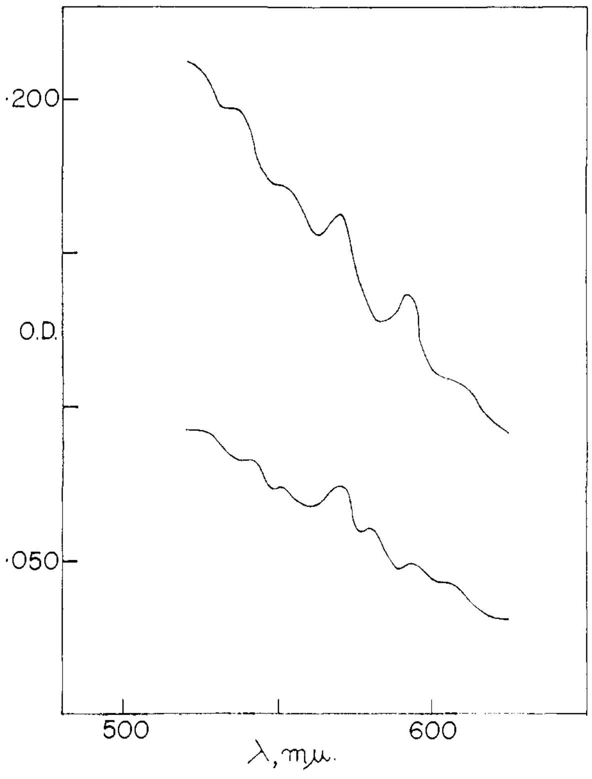

Fig. 1.—Absorption spectrum of a solution prepared by adding 0.22 ml. of a 1.5 × 10^{-2} M acetone solution of menadione to 1.0 ml. of a solution of the halogenated tyrosine in half saturated aqueous $KHCO_3$. The latter solution was 9.7 × 10^{-2} M in the case of 3,5-diiodotyrosine (upper curve) and 6.6 × 10^{-2} M in the case of 3,5-dibromotyrosine. Blank: similar solutions omitting the vitamin; optical path, 1 cm.; room temperature. Readings were taken from right to left as fast as possible.

Since charge transfer bands are quite diffuse—as demanded by theory[2]—the fine structure must belong to another band which is presumably overlapped by the electron transfer absorption. This band may be ascribed to the T←S transition in the quinone which is expected in the region of the fine structure[3,4] and greatly enhanced by the spin-orbit coupling effect of the iodine atoms. Confirmation is given by the set of reasonably well resolved bands also presented by the bromo analog without any spectral shift (Fig. 1). Phenolate does not induce any absorption in this region. In acetone-aqueous $KHCO_3$ half saturated (1:5 v./v.) at 25°, the association constant and the molar extinction coefficient at 520 mμ for the 3,5-dibromotyrosine-menadione complex are 1.1 l. mole^{-1} and 850; for the iodo complex the values are 1.4 l. mole^{-1} and 800.

Very interestingly also, the absorption band due to the interaction of halogenated quinones with hexamethylbenzene shows some fine structure.[5]

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[1] A related, unpublished work was presented at the International Biophysics Congress, Stockholm, 1961, Abstracts of Contributed Papers, p. 89.

[2] S. P. McGlynn, *Chem. Revs.*, **58**, 1113 (1958). Several important references concerning the subject of this communication are given in that review article.

[3] J. W. Sidman, *J. Am. Chem. Soc.*, **78**, 2363, 4567 (1956).

[4] A. Kuboyama, *Bull. Chem. Soc. Japan*, **35**, 295 (1962).

[5] R. Foster, D. L. Hammick and P. J. Placito, *J. Chem. Soc.*, 3881 (1956). The fine structure in the peak of the complex of *p*-benzoquinone near 420 mμ may be connected with another transition of the quinone; see for instance, ref. 4.

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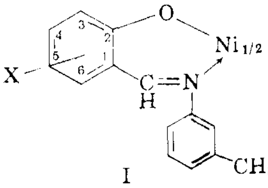
N.M.R. CONTACT SHIFTS IN PARAMAGNETIC NICKEL(II) SALICYLALDIMINES

Sir:

Distinct advantages in mapping unpaired electron distributions in paramagnetic species by n.m.r. contact shifts rather than by e.p.r. hyperfine splittings have been demonstrated by studies of the nickel(II) chelates of the aminotroponeimines.[1,2,3] It has now been found that large high and low field shifts are also observed in the proton n.m.r. of the paramagnetic[4] nickel(II) chelates of N-*m*-tolylsalicylaldimines, I. These shifts are attributed to



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contact interaction between protons and spin densities centered on ring carbon atoms. This spin density arises as a result of delocalization of the fractional unpaired electron placed on nitrogen and oxygen by dπ-pπ bonding with nickel. For this non-alternant system contributions to the ground state wave function from valence bond structures such as B and C are expected to place positive spin density at C_3 and C_5. Negative spin densities aris-

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[1] W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, **33**, 607 (1960).

[2] R. E. Benson, D. R. Eaton, A. D. Josey and W. D. Phillips, *J. Am. Chem. Soc.*, **83**, 3714 (1961).

[3] D. R. Eaton, A. D. Josey, W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).

[4] R. H. Holm and T. M. McKinney, *J. Am. Chem. Soc.*, **82**, 5506 (1960).