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.

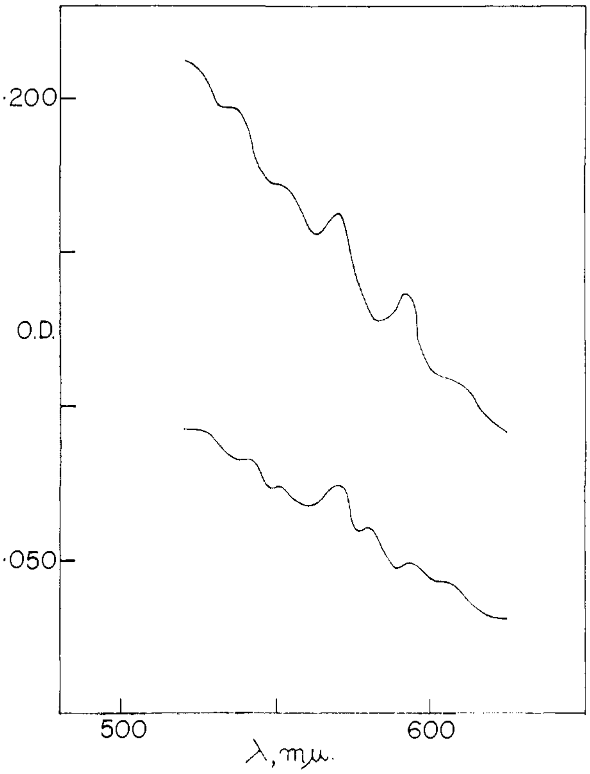

Fig. 1.—Absorption spectrum of a solution prepared by adding 0.22 ml. of a 1.5 × 10^{-2} *M* acetone solution of menadione to 1.0 ml. of a solution of the halogenated tyrosine in half saturated aqueous $KHCO_3$. The latter solution was 9.7 × 10^{-3} *M* in the case of 3,5-diiodotyrosine (upper curve) and 6.6 × 10^{-3} *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]

Acknowledgment.—We wish to thank the Rockefeller Foundation and the "Conselho Nacional de Pesquisas" for grants, and the latter also for a fellowship awarded to M. B.

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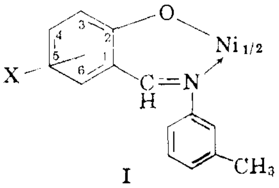
N.M.R. CONTACT SHIFTS IN PARAMAGNETIC NICKEL(II) SALICYLALDIMINES

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 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).

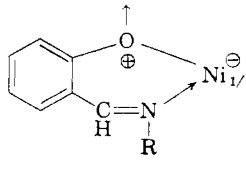
TABLE I

N.M.R. PROTON RESONANCE FREQUENCIES[a] FOR I

Substituent X	4	5	6	CH=N	*ortho*	*meta*	*meta* CH_3	*para*
H[c]	−1890	+275	−1292	....	~+200	−810	+96[b,d]	+181
	(− 9.77)[c]	(+4.64)	(− 5.79)		(broad)	(−2.58)		(+4.01)[c]
4-CH_3	+ 307[d]	+286	−1275	....	...	−792	+91[d]	+178
5-CH_3	−1925	−917[d]	−1258	~−3490	~+250	−799	+91[d]	+186
				(broad)	(broad)			
H[e]	−1884	+272	−1306	....		−772	+102	−701[d]
H[f]	−1892	+271	−1319	....	~+250	+ 96[d]	+96[d]	+179
		ortho −338						
5-C_6H_5-N=N-	−1925	*meta* −461	−1525	....	~+250	−805	+92[d]	+175
		para −300			(broad)			

[a] In c.p.s. at 60 Mc./sec. The chelate spectra were determined in CS_2 solution and were internally referred to tetramethylsilane. For the ligands in $CDCl_3$, these resonance frequencies are applicable: −135 (CH_3), −420 (aromatic protons) and −504 (-CH=N). [b] Integration of the N-(*m*-CH_3) resonance suggests that it includes the 3-H resonance [c] Spin densities × 10^3 are given in parentheses for this compound. [d] Q_{CH_3}: 4-CH_3 = +6.8 gauss, 5-CH_3 = +25.3 gauss, N-(*m*-CH_3) = +13.8 gauss, N-(*p*-CH_3) = +21.2 gauss. [e] Data for bis-[N-(3′,4′-dimethylphenyl)-salicylaldimine]-nickel(II). [f] Data for bis-[N-(3′,5′-dimethylphenyl)-salicylaldimine]-nickel(II).

ing from electron correlation effects are expected at C_4 and C_6. Consistent with this prediction, protons attached to C_3 and C_5 exhibit high field resonances, and protons attached to C_4 and C_6 exhibit low field resonances.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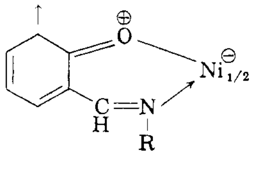
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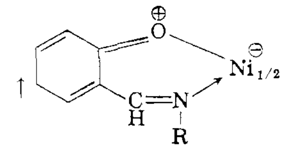
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Although the proton resonances of the salicylaldimines are considerably broader than those of the aminotroponeimineates and nuclear spin–spin structure cannot be resolved, it has been possible to make spectral assignments of the individual protons on the salicylaldehyde residue through substitution studies. The frequencies are given in Table I. For I, X = H,[5] the spin density[6] at C_5 is about 0.1 that of the γ position of an aminotroponeimineate.[2,3] On substituting CH_3 at C_5, proton shifts for methyl are observed that are in an opposite direction from that of the C_5 proton. Furthermore, the ratio $|a_{CH_3}/a_{CH}|$ of 1.125 is close to that observed in e.p.r. studies of methylquinone/quinone ion radicals[7] and corresponds to Q_{CH_3} = +25.3 gauss. This result indicates that, at least at the C_5 position, the spin density is moving primarily through the π-system. Moreover, on substituting the phenylazo group for hydrogen at C_5 an alternation of spin density signs on the phenyl ring is observed, and the attenuation from C_5 to the para position is 6.8. The relative spin densities and the attenuation are comparable to those observed for the same substituent on an aminotroponeimineate,[3] substantiating that the electron is moving through the π-system in both of these structures.

For I, X = 4-CH_3, the shifts for CH_3 at C_4 and C_{meta} of the N-phenyl substituent, which are sites of negative spin density, are opposite those of the protons at these positions, in accord with the direct contact interaction mechanism (hyperconjugation). The ratios $|a_{CH_3}/a_{CH}|$ are less than those found for the C_5 position, a site of positive spin density, and correspond to Q_{CH_3} values of +6.8 gauss (C_4) and +13.8 gauss (C_{meta} of phenyl ring).[8] The results imply a stronger hyperconjugation effect at the latter position.

Magnetic susceptibility studies in carbon disulfide solution at room temperature of several of the N-*m*-tolyl derivatives have given magnetic moments of ~3.4 B.M. in accord with two unpaired electrons on nickel. In chloroform, the magnetic moment of I, X = 4-CH_3, has been found to be temperature independent over −60 to +50°.

A simple valence bond calculation was carried out for I, X = H, assuming one electron delocalized. Comparison of calculated with experimental spin density distributions suggests that approximately one-sixtieth of an unpaired electron has transferred from nickel to each salicylaldimine ligand. This value of spin transfer in the nickel(II) salicylaldimines is to be compared with the transfer of one-tenth of an electron to each ligand in the nickel(II) aminotroponeimineates.[3]

As found independently by Holm,[9] molecular weight studies on I, X = H, have shown that this compound is associated in solution. Similar studies in the case of I, X = 3-CH_3, indicate that essentially no association is occurring up to 0.042 molal concentration in benzene, presumably due to steric hindrance. Furthermore, the latter compound is diamagnetic ($\mu_{eff} \leqslant 0.1$ B.M.) and, as expected, no contact shifts are observed.

The magnetic susceptibility of the nickel chelate of N-methylsalicylaldimine is reported to vary with

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(5) Initially prepared by L. Hunter and J. A. Marriott, *J. Chem. Soc.*, 2000 (1937).

(6) Calculated by the method described in ref. 2.

(7) A. D. McLachlan, *Mol. Phys.*, 1, 233 (1958).

(8) A similar observation has been made in nickel(II) aminotroponeimineates. For the N-phenyl derivatives, $|a_{CH_3}/a_{CH}|$ at the para position corresponds to Q_{CH_3} = +27.7 gauss, whereas $|a_{CH_3}/a_{CH}|$ at the meta position corresponds to Q_{CH_3} = +8.3 gauss (unpublished results).

(9) We wish to thank Dr. Holm for making his result available to us prior to publication.

concentration.[10] In accord with these observations, we have noted large proton shifts for this compound that are concentration dependent.

Finally, we have observed large changes in the n.m.r. spectra of several nickel chelates of salicylaldimines on the addition of pyridine together with corresponding shifts in the proton resonances of pyridine. Such effects are consistent with a coordination of pyridine to nickel and studies are being continued.

The chelates prepared for this study were obtained either by treating the Schiff base phenolate ion with nickel acetate or, more conveniently, by treating a suspension of the bis-(salicylaldehyde)-nickel(II) in boiling ethanol with an excess of the substituted aniline.[11,12] The chelates were obtained as anhydrous solids and had satisfactory C, H, N and Ni analyses.

[10] R. H. Holm, *J. Am. Chem. Soc.*, **83**, 4683 (1961).

[11] F. Basolo and W. R. Matoush, *ibid.*, **75**, 5663 (1953).

[12] L. Sacconi, P. Paoletti and G. Del Re, *ibid.*, **79**, 4062 (1957).

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THE PHOTODIMERIZATION OF MONOMETHYL FUMARATE

Sir:

Through the courtesy of Dr. G. W. Griffin we have had access to his work (since published[1,2]) on the photodimerization in the solid state of fumaric acid derivatives to the corresponding cyclobutanes. Following our own interest in the photodimerization of cinnamic acids to α-truxillic and β-truxinic acids and the dependence of the stereochemical course of this reaction on the lattice geometry of the monomer,[3] we have extended Griffin's work on the fumaric derivatives by crystallographic studies. As Griffin, *et al.*, have already noted the packing arrangements of dimethyl fumarate[4] and of fumaronitrile[5] (see Table I) favor the formation of dimers of symmetry 2/m through the contact of parallel molecules along the shortest translation period of 4 Å.

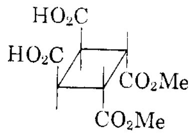
TABLE I

trans-Compound	a, Å.	b, Å.	c, Å.	α	β	γ	Space group	n
$MeO_2CCH{=}CHCO_2Me$[4]	3.92	9.24	5.93	101° 47′	112° 49′	109° 20′	$P\bar{1}$	1
$NCCH{=}CHCN$[5]	3.89	5.60	11.54	...	121.9°	...	$P2_1/n$	2
$MeO_2CCH{=}CHCO_2H$	14.14	3.99	5.60	72.6°	98.8°	83.8°	$P\bar{1}$	2
β-$PhCH{=}CHCO_2H$	6.05	4.04	31.3	...	90.3°	...	$P2_1/c$	4
$MeO_2C(CH{=}CH)_2CO_2Me$	7.74	5.81	5.82	88.0°	121.8°	106.1°	$P\bar{1}$	1
$MeO_2C(CH{=}CH)_3CO_2Me$	7.60	5.99	13.06	81.4°	107.7°	105.9°	$P\bar{1}$	2

A crystallographic survey of other fumaric acid derivatives shows that monomethyl fumarate crystallizes in a packing arrangement similar to that of the diester. It was therefore of interest to test its photo-behavior, which had not been reported by Griffin. Ultraviolet irradiation of a powdered sample of monomethyl fumarate produced a progressive change in the X-ray powder pattern. After several days of exposure the irradiated sample was washed free from starting material with diethyl ether; the less soluble residue showed no hydrogen uptake on attempted catalytic hydrogenation. After recrystallization from di-*n*-butyl ether this material melted at 153–154°; elemental analysis gave: C, 46.5; H, 4.4; (O) CH_3, 11.5. Calcd. for $C_{10}H_{12}O_8$: C, 46.2; H, 4.7; (O) CH_3, 11.6.

A convenient method of isolation of the dimeric material treats the irradiated sample with excess boiling thionyl chloride which removes the monomer at the water pump as the volatile β-(chloroformyl) methylacrylate. The anhydride of the dimer (m.p. 144° from chloroform) gives an infrared spectrum characteristic of a five-membered cyclic anhydride. Hydrolysis with hot water regenerates the diacid diester of m.p. 153–154°.

The photodimer as well as its anhydride were converted by methanolic hydrogen chloride to a compound identical with cyclobutane 1,2,3,4-tetracarboxylic acid tetramethyl ester of m.p. 144–145° obtained by Griffin and co-workers by the photodimerization of dimethyl fumarate.[2] The conformation of the dimer of monomethyl fumarate is therefore established as I. Thus, the crystal structures of the three monomers have in common a shortest axis of 4 Å. and dimerization to dimers of symmetry *m;* they are completely analogous to the β-modification of substituted cinnamic acids defined by shortest axes of 4.0 ± 0.1 Å. and photodimerization to β-truxinic acids.



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The next higher homologs, dimethyl *trans,trans*-muconate and dimethyl *all-trans*-hexatriene dicarboxylate, do not belong to this structure type (*see* Table I); work on their photochemical behavior is under way.

Acknowledgment.—We wish to thank Mr. L. Leiserowitz and Mr. D. Rabinovich for measuring some of the crystallographic constants reported here.

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[4] I. E. Knaggs and K. Lonsdale, *J. Chem. Soc.*, 417 (1942).

[5] B. Post, *private communication*.

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