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PARAMAGNETIC RESONANCE OF NEW ORGANIC RADICALS

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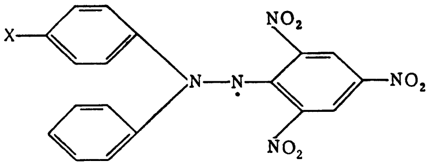
THE narrow line-width of the resonant absorption curve of the organic radical α,α-diphenyl β-picryl hydrazyl has been explained by exchange interaction of the odd electron in the $-N-N$ group.[1] Direct confirmation of the existence of the exchange interaction was obtained from studies of hyperfine structure of this absorption line.[2]

We undertook a set of experiments with an object to investigate the influence of substitutes X in para-position of the α-phenyl ring on exchange interactions in organic radicals. Para-fluoro-, para-chloro-, para-bromo-, and para-methoxy-derivatives of hydrazyl were investigated. Three of these (the para-fluoro-, para-chloro-, and para-methoxy-derivatives) were obtained first.



The line shape of the paramagnetic resonant absorption,[3] characterized by the ratio of fourth to the second moment of the resonant curve, M_4/M_2, served to determine the magnitude of exchange interactions. This ratio was obtained by numerical integration of the experimental absorption curve. The moments were computed separately for the left and right half of the curve and average values were taken.

Substitute X	g-factor	M_4/M_2	ΔH	A
H	2,0042 ± 0,0004	1,43±0,02	1.0 ± 0.15	300
Cl	2,001 ± 0,001	1,42±0.02	1.2 ± 0.15	290
Br	2,002 ± 0,002	1,40±0.02	2.2 ± 0.15	170
OCH_3	2,000 ± 0,002	1,30±0.02	2.6 ± 0.2	120
F	2,000 ± 0,004	small	4.1 ± 0.5	20

Measurement of the paramagnetic resonance absorption was performed using Zavoiskii's grid-current method.[4] To obtain absorption curves without admixture of dispersion, the generator circuit was coupled very weakly to the measuring coil. The generator frequency was varied in a fairly narrow region about a resonant frequency of 621 Mcs and was measured by a type 3003 heterodyne detector with an accuracy of 0.005%. A signal modulated at 224 cps was fed through a broad-band amplifier with a bandwidth 30 cps to 10 Mcs into an oscilloscope or into a narrow-band amplifier of bandwidth 5 cps and a synchronous detector with meter. Absorption curves were photographed from the screen of the oscilloscope. The narrow-band system was used for observing the width of the absorption curve between the points of steepest slope. The measured quantities were the maximum values A of the absorption curves, which yield values proportional to χ''. All the samples investigated contained equal molar amounts of radicals. The field was calibrated against the known resonance of α,α-diphenyl-picryl-hydrazyl, whose g-factor was taken to be 2.0042 ± .0004.[1]

The results are given in the table. It is seen that all the quantities, except the g-factor, which differs only slightly from 2, change gradually from H to F. The exchange interaction thus diminishes in the transition from H to F.

Visible and ultraviolet spectra were also measured for all compounds, using SF-2 and SF-4 equipment. In the visible part of the spectrum all the radicals investigated show absorption maxima at 520 mμ, and the maximum absorption decreases in the same manner as at radio frequencies. No sharp maxima were found in the ultraviolet spectral region.

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ASYMPTOTIC SELECTION RULES FOR BETA DECAY OF DEFORMED NUCLEI

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It was shown in a number of investigations[1-6] that for particle transitions in deformed nuclei one must take into account not only the selection rules for the total angular momentum I and parity π but also the selection rules for asymptotic quantum numbers Λ, Σ, and also N and n_z (or n_z and $n_\perp$) introduced by Nilsson.[7] Λ and Σ are quantum numbers of the projection of orbital and spin angular momenta on the elongation axis of the nucleus (the z-axis); $\Lambda + \Sigma = \Omega$, where Ω is the quantum number of the projection of the total angular momentum of the particle on the z-axis; N is the principal quantum number of the oscillator, and n_z and $n_\perp$ are the quantum numbers of nuclear oscillations along the z-axis and in the plane normal to the z-axis respectively.

Type	Matrix Element	$k = \Delta\Omega = \Delta J$	$\Delta\Lambda$	$\Delta\Sigma$	Δn_z	ΔN
S, V	$\int y_{\lambda k}(\mathbf{r})$	$\pm\lambda$	$\pm\lambda$	0	0	$\lambda, \lambda-2, \ldots -\lambda$
V	$\int y_{\lambda k}(\nabla)$	$\pm\lambda$	$\pm\lambda$	0	0	$\lambda, \lambda-2, \ldots -\lambda$
T, A	$\int y_{\lambda+1 k}(\sigma)$	$\pm\lambda$ $\pm\lambda$ $\pm(\lambda+1)$	$\pm(\lambda-1)$ $\pm\lambda$ $\pm\lambda$	±1 0 ±1	±1 0 0	$\lambda, \lambda-2, \ldots -\lambda$
T, A	$\int y_{\lambda k}[\sigma\mathbf{r}]$	$\pm\lambda$	$\pm(\lambda-1)$ $\pm\lambda$	±1 0	±1 0	$\lambda, \lambda-2, \ldots -\lambda$
T	$\int y_{\lambda k}[\sigma\nabla]$	$\pm\lambda$	$\pm(\lambda-1)$ $\pm\lambda$	±1 0	±1 0	$\lambda, \lambda-2, \ldots -\lambda$

In this work selection rules for asymptotic quantum number N, n_z, Λ, Σ are established for β-transitions of an arbitrary order of forbiddenness ($\lambda > 1$) for different types of interactions. (Allowed and singly-forbidden transitions were considered by Alaga.[1]) The table gives the results of the calculations. The first column in the table shows the type of interaction — S, V, T, or A. For all transitions except $\lambda = 1$ the pseudoscalar interaction gives only small corrections to the matrix elements of transitions of $(\lambda - 2)$-fold forbiddenness. The second column gives the matrix elements of interaction operators in a non-relativistic approximation. Spherical representation is chosen.[8] Here

$$y_{\lambda k}(\mathrm{x}) = (i/\lambda\hbar)\,\mathrm{x}\,\{\mathrm{p}y_{\lambda k}(\mathrm{r})\}, \quad \mathrm{x} = \sigma,\ \nabla,\ [\sigma\mathrm{r}],\ [\sigma\nabla], \qquad y_{\lambda k}(\mathrm{r}) = r^\lambda Y_{\lambda k}(\vartheta, \varphi).$$

The third column gives the selection rules for the total angular momentum I. Since in a strongly deformed nucleus the integral of motion is the projection of the total angular momentum on the elongation axis, we let $\Delta I = \Delta\Omega = k$. Thus the rotational and the K-forbidden modes are excluded. Next two columns give the selection rules for Λ and Σ. These, of course, are related to the data of the preceding column (the condition $\Delta\Lambda + \Delta\Sigma = \Delta\Omega$ must be satisfied). Let us note that for scalar or vector interactions only those transitions can take place for which the projection of the spin of the particle on the elon-