EFFECT OF STERIC FACTOR ON ELECTRON EXCHANGE IN PARAMAGNETIC DERIVATIVES OF ISOPHTHALIC ACID

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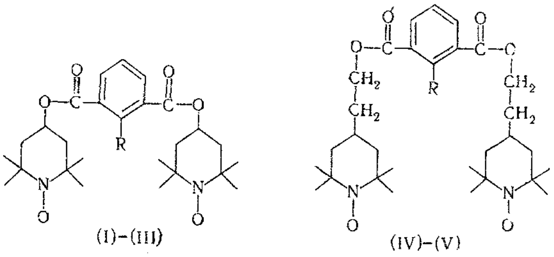
Previously we had reported that the EPR spectra of the isomeric biradicals obtained from the phthalic, isophthalic, and terephthalic acids possess a distinctive hyperfine structure in dilute solutions [1-4]. The most interesting, and at the same time the least studied, are those biradicals in which the frequencies of electron exchange are commensurate in the order of magnitude of the values with the frequency of the contact coupling. To such radicals belong the paramagnetic isophthalates of structure (I)-(V)


(I)-(III) (IV)-(V)

—R = H (I) (IV); CH_3 (II); n-C_4H_9 (III); (V)

When a dilute solution of biradical (I) is heated up to 130-150° its initial three-component spectrum (Fig. 1a) is transformed to a five-component spectrum (Fig. 1b) due to an increase in the intensity of the vibrational – rotational motions of the ester groups, which, in turn, leads to an increase in the frequency of the paired convergences of the iminoxyl fragments and, as a result, to more intense electron exchange.

The present paper includes the synthesis and study of those isophthalates in which the 2 position of the aromatic ring is occupied by hydrocarbon substituents that are capable of preventing convergence of the N$\dot{-}$O groups. The experiments disclosed that even for biradical (II) the electron exchange is not manifested even above 150°. The hyperfine structure of the EPR spectra indicates that the iminoxyl groups are disconnected in this case. When the 2,2,6,6-tetramethyl-1-oxyl-4-piperidyl fragments in the isophthalates are replaced by 2,2,6,6-tetramethylpiperidyl-1-oxyl-4-β-ethyl fragments the EPR spectra are radically changed, since the freedom of the intramolecular vibrational – rotational motions of the iminoxyl groups increases. Thus, biradicals (IV) and (V), even at room temperature, have a hyperfine structure of the EPR spectra that is characteristic for biradicals with a fast electron exchange (Fig. 1c, d). These results make it possible to assume that in the case of a sufficient length and lability of the bridges, connecting the paramagnetic centers, in the biradicals the convergenc of the iminoxyl groups is energetically favorable even if certain steric hindrances are present.

The molecular models of biradicals (III) and (V), depicted in Fig. 2, are found to be in agreement with the above given interpretation of the experimental data.

EXPERIMENTAL METHOD

2-Butylisophthaloyl Dichloride. The dichloride was obtained in conventional manner [5], in 80% yield, by heating 2-butylisophthalic acid with an excess of freshly distilled thionyl chloride; bp 85-87° (0.1 mm); n_D^{20} 1.5500. Found: C 55.75; H 4.41; Cl 27.45%. $C_{12}H_{12}O_2Cl_2$. Calculated: C 55.60; H 4.67; Cl 27.35%.

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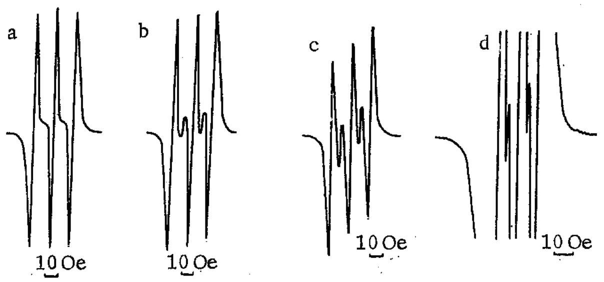

Fig. 1. EPR spectra of dilute heptane solutions of biradicals: a) (I) at 22°; b) (I) at 163°; c) (IV) at 22°; d) (V) at 22° (in the absence of oxygen).

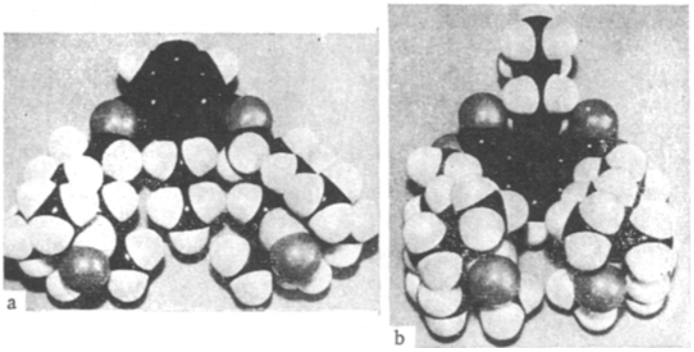

Fig. 2. Stuart – Briegleb molecular models of biradical (V): a) the 2-n-butyl substituent sterically hinders electron exchange; b) the substituent does not prevent initiation of electron exchange between the paramagnetic centers of the =N – O groups.

2-Methylisophthaloyl Dichloride. The dichloride was obtained under the conditions of the preceding experiment, in quantitative yield, from 2-methylisophthalic acid [6]; mp 92° (from hexane).

Di-(2,2,6,6-tetramethyl-1-oxyl-4-hydroxypiperidyl)-2-methylisophthalate (II). To a solution of 1 g of 2,2,6,6-tetramethyl-4-hydroxypiperidyl-1-oxyl in 20 ml of anhydrous benzene and 5 ml of triethylamine was added in drops a solution of 0.5 g of 2-methylisophthaloyl dichloride in 25 ml of anhydrous benzene. After stirring for 2 days the precipitate was filtered, the filtrate was evaporated to dryness, and the solid residue was chromatographed on Al_2O_3 (eluant: chloroform – ethyl acetate, 4 : 1), collecting the bottom colored zone. Evaporation of the solvent and recrystallization from heptane gave 0.73 g (64.7%) of (II) with mp 139-140°. Found: N 5.67%; mol. wt. 488. $C_{27}H_{40}N_2O_6$. Calculated: N 5.73%; mol. wt. 488.631.

Di-(2,2,6,6-tetramethyl-1-oxyl-4-hydroxypiperidyl)-2-n-butylisophthalate (III). Using the above-described method, from 3 g of 2,2,6,6-tetramethyl-4-hydroxypiperidyl-1-oxyl in 40 ml of anhydrous benzene and 7 ml of triethylamine, and 1.85 g of 2-butylisophthaloyl dichloride, was obtained (III) in 82% yield as two kinds of crystals, which underwent mutual interchange when heated. Needles, mp 95-96.5°. Found: C 68.08; H 8.90; N 5.44%; mol. wt. 530. Rhombic crystals, mp 108°. Found: C 67.84; H 8.80; N 5.47%; mol. wt. 530. $C_{30}H_{46}N_2O_6$. Calculated: C 67.89; H 8.74; N 5.25%; mol. wt. 530.

Di-(2,2,6,6-tetramethyl-1-oxyl-4-β-hydroxyethylpiperidyl)isophthalate (IV). Using the method to obtain (II), from 1 g of 2,2,6,6-tetramethyl-4-β-hydroxyethylpiperidyl-1-oxyl, 0.4 ml of absolute pyridine and 0.5 g of isophthaloyl dichloride in 20 ml of anhydrous benzene was isolated a dark red oil, which failed to crystallize on long standing in the refrigerator. The yield of (IV) was 81.1%; R_f 0.4 ($CHCl_3$). Found: C 68.24; H 8.83; N 5.32%. $C_{30}H_{46}O_6N_2$. Calculated: C 67.89; H 8.74; N 5.25%.

Di-(2,2,6,6-tetramethyl-1-oxyl-4-β-hydroxyethylpiperidyl)-2-n-butylisophthalate (V). In a similar manner, from 1 g of 2,2,6,6-tetramethyl-4-β-hydroxyethylpiperidyl-1-oxyl and 0.512 g of 2-butylisophthaloyl dichloride was obtained a dark red oil, which failed to crystallize on standing in the refrigerator. The yield of (V) was 94.2%; R_f 0.35 ($CHCl_3$). Found: N 4.95%. $C_{34}H_{46}O_6N_2$. Calculated: N 4.76%.

The EPR spectra were recorded on an EPR-3 spectrometer.

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CONCLUSIONS

1. The di-2,2,6,6-tetramethyl-1-oxyl-4-hydroxypiperidyl esters of the 2-methyl- and 2-n-butylisophthalic acids, and the di-2,2,6,6-tetramethylpiperidyl-1-oxyl-4-β-hydroxyethyl esters of the isophthalic and 2-n-butylisophthalic acids, were synthesized.

2. A study was made of the hyperfine structures of the EPR spectra of the obtained biradicals.

LITERATURE CITED

1. E. G. Rozantsev, V. A. Golubev, M. B. Neiman, and Yu. V. Kokhanov, Izv. AN SSSR, Ser. Khim., 572 (1965).
2. E. G. Rozantsev and V. A. Golubev, Izv. AN SSSR, Ser. Khim., 718 (1965).
3. E. G. Rozantsev, Free Nitroxyl Radicals, Plenum Press, New York – London (1970).
4. E. G. Rozantsev, V. A. Golubev, and M. B. Neiman, Izv. AN SSSR, Ser. Khim., 393 (1965).
5. F. M. Stoyanovich, R. G. Karpenko, and Ya. L. Gol'dfarb, Zh. Organ. Khim., 5, 2005 (1969).
6. R. G. Karpenko, F. M. Stoyanovich, S. P. Raputo, and Ya. G. Gol'dfarb, Zh. Organ. Khim., 6, 112 (1970).