CONCLUSIONS

1. Dithiolane diiron hexacarbonyl complexes are formed in the reaction of S_8 with $Fe_3(CO)_{12}$ in the presence of cyclohexene or 1-hexene. When cyclohexene is used, sulfur atoms are incorporated at the double bond to give cyclic polysulfides.

2. The structure of thiotriiron decarbonyl was investigated by means of x-ray diffraction analysis.

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SPIN EXCHANGE IN PARAMAGNETIC BENZENEPOLYCARBOXYLATES

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The synthesis of the first unconjugated nitroxyl biradical, whose ESR spectrum indicates coupling of the strongly localized radical centers (RC), in our laboratory in 1965 [1] has served as the basis for the study of the chemical physics of bi- and polyradicals [2]. Recent interest in this field has arisen in regard to the use of biradicals as spin labels and probes [3]. While the spin-exchange behavior in the biradicals is sufficiently understood [4, 5], spin exchange in polyradical systems has been the subject of considerably fewer studies. Thus, in the benzenepolycarboxylic acid series, only the paramagnetic esters of trimesic and pyromellitic acids have been studied. Analysis of the ESR spectra of these compounds indicated the participation of all the radical centers in the spin exchange at high temperatures [6].

We have undertaken a study of spin exchange in polyradicals. The paramagnetic esters of benzenepolycarboxylic acids, namely, hemimellitic (I), trimellitic (II), prehnitic (III), mellophanic (IV), pyromellitic (V), benzenepentacarboxylic (VI), and mellitic (VII) acids, were taken as models



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Fig. 1. ESR spectra of triradical (II) at 1) -40; 2) 60; 3) 100; 4) 110; 5) 132; 6) 155°C.

Fig. 2. ESR spectra of tetraradical (III) at 1) -60; 2) -20; 3) 40; 4) 60; 5) 70; 6) 155°C.



Compounds (I)-(IV), (VI), (VII) were prepared by the action of the corresponding acid chlorides on 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-oxyl (VIII), while compound (V) was obtained by the transesterification of the tetramethyl ester of pyromellitic acid by alcohol-radical (VIII).

The ESR spectra of toluene solutions of polyradicals (I)-(VII) were studied at -60 to 160° C. At low temperatures, the ESR spectra of (II)-(V) are a 1:1:1 triplet resulting from the autonomous interaction of each unpaired electron with the ¹⁴N nucleus of its radical fragment (monoradical spectra) and indicate the lack of intramolecular spin exchange. The temperature changes of the spectra of polyradicals (II)-(V) differ and indicate the consecutive inclusion of two, three, and four radical centers in spin exchange.

The ESR spectrum of triradical (II) in the range from -40 to 80°C shows an alternatively broadened quintuplet, indicating effective spin exchange between the ortho-RC (Fig. 1). Upon further temperature elevation, the quintuplet is transformed into a septuplet with broadened components $m_T = \pm 1$ and ± 2 , which indicates the involvement of a third RC in spin exchange.

The ESR spectrum of tetraradical (III) shows an alternatively broadened quintuplet even at -60° C. At 40° C, the component intensity ratio is close to binomial (1:2:3:2:1). This finding indicates effective pairwise participation of RC in spin exchange (exchange between the RC in the 1,2 and 3,4 positions). Upon further temperature elevation, the quintuplet is transformed into a nine-line spectrum, which indicates effective exchange between all four RC (Fig. 2).

In the case of tetraradical (IV) (Fig. 3), superposition of a septuplet spectrum due to spin exchange of the three RC in positions 1, 2, 3 and of the triplet spectrum of the RC in position 5 is found in the narrow range from -40 to -20° C. Upon further temperature elevation, the septuplet components with m_I = ±1 and ±2 are shifted and the spectrum acquires nine-line character, indicating interaction of all four RC.



Fig. 3. ESR spectra of tetraradical (IV) at 1) -60; 2) -20; 3) 20; 4) 40; 5) 60; 6) 150°C. Fig. 4. ESR spectra of tetraradical (V) at 1) -60; 2) -20; 3) 40; 4) 80; 5) 120; 6) 180°C.

The temperature-dependent changes in the ESR spectra of tetraradical (V) (Fig. 4) are reminiscent of polyradical (III). The triplet is converted into a quintuplet at -20°C and the quintuplet is transformed above 60° C into a nine-line spectrum, indicating participation of all four RC in the exchange. Since the line intensity ratio in the quintuplet is close to binomial, there clearly is pairwise spin exchange for the RC in positions 1,2 and 4,5 at -20 to 60° C.

The spin-exchange behavior for polyradicals (I), (VI), and (VII) is similar. The ESR spectrum of triradical (I) (Fig. 5) at from -60 to 180°C is a septuplet, indicating effective spin exchange of all three RC. The septuplet is transformed into an exchange-broadened singlet below -60°C.

The ESR spectra of pentaradicals (VI) (Fig. 6) and hexaradicals (VII) (Fig. 7) are broad single lines which are transformed into multiplets characteristic for effective spin exchange of the five and six RC only at rather high temperatures. The dense packing of the RC in (I), (VI), and (VII) apparently is conducive for effective spin exchange in a broad temperature band.

Analysis of the line width in the ESR spectra of (II)-(V) permits evaluation of the kinetic parameters for spin exchange with the participation of two, three, or four RC. Several conformations are apparently possible for such complex systems. These conformations are characterized by different effectiveness of the exchange processes. Rigorous analysis of such systems involving multiple conformations is difficult, and thus we examined spin exchange in the framework of a two-conformation model with intense rapid exchange [4]. This approach is rather common in examining biradicals with ESR spectra characterized by an alternatively broadened quintuplet. In this approximation, the observed line broadening may be described by an effective exchange frequency (v_{exc}) which determines the frequency of collisions of RC leading to rapid modulation of spin coupling due to intramolecular motion. In the polyradicals examined, such motions are rotation of the RC relative to the ester bridges connecting these RC with the benzene ring. The exchange frequencies within the framework of the two-conformation by the expression

 $v_{\rm exc} = \Delta \omega^2 / 4 \Delta (1/T_2)$

where $\Delta \omega$ is the distance between the exchanging lines in frequency units, rad/sec; and $\Delta(1/T_2)$ is the exchange contribution to line width.

Figure 8 shows the Arrhenius plots for the exchange frequencies of two RC (analysis of the biradical spectra). The close-to-linear dependence indicates the validity of the two-



conformation model for the exchange of two RC. Table 1 shows that the kinetic parameters for the pairwise interaction of the RC are rather similar for radicals (II), (III), and (V), which indicates a similarity in conformations, between which exchange of the two RC occurs.

We attempted to extend the two-conformation model for spin exchange to analysis of the exchange interaction of three and four RC. For example, we may propose for (IV) that spin exchange occurs due to transition between a conformation with the absence of exchange and a conformation, in which there is strong exchange directly between the three adjacent RC. In this case, the simultaneous overlap of the orbitals of the unpaired electrons of the three RC is likely unnecessary. Strong exchange between three RC may be achieved due to rapid consecutive collisions of the RC by a relay mechanism.

Analogous considerations may be used in examining the final step in the spin exchange between the three RC of (II) and four RC of (III), (IV), and (V). The amplitude and frequency of rotation of the RC apparently increase with increasing temperature, which permits overlap of the orbitals of unpaired electrons of distant RC. Taking account of the rapid relay transfer of spin coupling between adjacent RC relative to the exchange between distant RC, we may, in our opinion, use the two-conformation model in this specific case. The approximated RC with intense rapid exchange are considered as a single effective RC with $m_S = 1$ (II), (III), and (V) or $m_S = 3/2$ (IV) participating in spin exchange with distant RC. The satisfactory linearity of the Arrhenius plots for v_{exc} (see Fig. 8) of polyradicals (II)-(V) obtained from analysis of the alternatively broadened multiplets due to coupling of the unpaired electrons with the ¹⁴N nuclei also indicates the validity of the two-conformation model in



Fig. 7. ESR spectrum of hexaradical (VII) at 180°C.

Fig. 8. Arrhenius plots for the spin-exchange frequency (number of lines): 1) (II) (5); 2) (III) (5); 4) (V) (5); 1') (II) (7); 2') (III) (9); 3') (IV) (9); 4') (V) (9).

Poly- radical	V ₂₀	Vo	E,	Number of lines
	cm ⁻¹		kcal/mole	
(II) (III) (IV) (V)	$\begin{array}{c} 25 \cdot 10^{7} \\ 1,2 \cdot 10^{7} \\ 72 \cdot 10^{7} \\ 1,7 \cdot 10^{7} \\ 3 \cdot 10^{7} \\ 9,2 \cdot 10^{8} \\ 2,7 \cdot 10^{7} \end{array}$	$\begin{array}{c} 9,6\cdot10^{10}\\ 1,1\cdot10^{11}\\ 2,2\cdot10^{11}\\ 12,5\cdot10^{12}\\ 2,3\cdot10^{11}\\ 4,6\cdot10^{10}\\ 1.4\cdot10^{11}\end{array}$	2,96 5,33 2,8 7,9 5,2 2,3 5	5 7 5 9 9 5 9 5 9

TABLE 1. Kinetic Parameters for Spin Exchange in Polyradicals

this case.

Table 1 shows that the polyspin exchange frequencies are markedly lower, while the activation parameters are approximately doubled relative to those for the pairwise spin coupling, which satisfactorily corresponds to the proposed scheme for the exchange.

EXPERIMENTAL

The benzenepolycarboxylic acid chlorides were prepared by heating of the corresponding acids with PCI_5 [7]. The IR spectra were taken on a UR-20 spectrometer in KBr pellets and the ESR spectra were taken on a Varian E-12 spectrometer.

Tris(2,2,6,6-tetramethyl-1-oxyl-4-piperidyloxy) Hemimellitate (I). A sample of 0.65 g hemimellitic triacid chloride was added with stirring to a solution of 1.4 g (VIII) in 10 ml abs. pyridine with cooling to 0°C. The mixture was stirred for 1.5 h with cooling and for 20 h at $\sim 20^{\circ}$ C and then poured into 100 ml ice-water and acidified with dilute (1:10) HCl to pH 5. The precipitate was washed with water, dried, and subjected to chromatography on an alumina column with chloroform eluent. The lower colored zone was collected. After evaporation of the solvent, we obtained 0.9 g (59%) (I) with mp 179-180°C (from cyclohexane). Found, %: C 64.56; H 8.09; N 6.29. C₃₆H₅₄N₃O₉. Calculated, %: C 64.28; H 8.03; N 6.25. IR spectrum (ν , cm⁻¹): 1720 (CO), 1200-1240 (C=C), 1070-1220 (COC).

 $\frac{\text{Tris}(2,2,6,6-\text{tetramethyl-1-oxyl-4-piperidyloxy)} \text{ Trimellitate (II).} A \text{ yield of 1.38 g}}{(68\%) (II) \text{ with mp } 127-128^{\circ}\text{C} (\text{from cyclohexane}) \text{ was obtained analogously to (I) from trimellitic triacid chloride and 2 g (VIII). Found, %: C 64.70; H 8.10; N 6.35. C_{36}H_{34}N_{3}O_{9}. Calculated, %: C 64.28; H 8.03; N 6.25. IR spectrum (v, cm⁻¹): 1720 (CO), 1205-1240 (C=C), 1080-1120 (COC).}$

Tetrakis(2,2,6,6-tetramethyl-1-oxyl-4-piperidyloxy) Prehnitate (III). A sample of 0.8 g prehnitic tetraacid chloride was added with stirring to a solution of 2 g (VIII) in 10 ml abs. pyridine and 15 ml abs. benzene with cooling to 0°C. The mixture was stirred for 1 h with cooling and for 18 h at \sim 20°C, then poured into ice water, and the organic layer was removed and dried over sodium sulfate. The solvent was evaporated and the residue was subjected to chromatography on a 100/160 silica gel column with chloroform eluent. The lower colored zone was collected, which, after evaporation of the solvent, gave 1.9 g (87.5%) (III), mp 223-224°C (from isopropyl alcohol). Found, %: C 63.43; H 8.16; N 6.33. C_{4.6}H₇₀N₄O₁₂. Calculated, %: C 63.44; H 8.04; N 6.43. IR spectrum (ν , cm⁻¹): 1725 (CO), 1200-1260 (C=C), 1070-1120 (COC).

<u>Tetrakis (2,2,6,6-tetramethyl-1-oxyl-4-piperidyloxy) Mellophanate (IV)</u>. A sample of 2.3 g (88.5%) (VI) was obtained with mp 188-189°C (from methanol) analogously to (III) from 1 g mellophanic tetraacid chloride and 2.5 g (VIII). Found, %: C 63.63; H 8.19; N 6.42. C4.6H70N4O12. Calculated, %: 63.44; H 8.04; N 6.43. IR spectrum (ν , cm⁻¹): 1735 (CO), 1200-1280 (C=C), 1105-1170 (COC).

Pentakis(2,2,6,6-tetramethyl-1-oxyl-4-piperidyloxy) Benzenepentacarboxylate (VI). A sample of 2.4 (77.3%) (VI) was obtained with mp 225°C (from ethanol) analogously to (III) from 1.1 g benzenepentacarboxylic pentaacid chloride and 3 g (VIII). Found, %: C 62.95; H 8.15; N 6.54. C₅₆H₈₆N₅O₁₅. Calculated, %: C 62.92; H 8.05; N 6.55. IR spectrum (v, cm⁻¹): 1735 (CO), 1200-1255 (C=C), 1105-1170 (COC). <u>Hexakis(2,2,6,6-tetramethyl-1-oxyl-4-piperidyloxy)</u> Mellitate (VII). A sample of 1.8 g (86.8%) (VII) was obtained with mp 228°C (from isopropyl alcohol) analogously to (III) from 0.8 g mellitic acid hexaacid chloride and 3.5 g (VIII). Found, %: C 62.42; H 8.25; N 6.57. $C_{66}H_{102}N_6O_{18}$. Calculated, %: C 62.55; H 8.06; N 6.63. IR spectrum (ν , cm⁻¹): 1740 (CO), 1205-1260 (C=C), 1080-1120 (COC).

Tetrakis (2,2,6,6-tetramethyl-1-oxyl-4-piperidyloxy) Pyromellitate (V). A sample of 0.7 g sodium ethylate was added to a solution of 1.5 g tetramethyl ester of pyromellitic acid and 4 g (VIII) in toluene and the mixture was heated at reflux until the liberation of methanol ceased (2.0-2.5 h). The reaction mass was poured into water and the organic layer was separated, dried over sodium sulfate, and evaporated. The residue was subjected to chromatography on a 100/160 silica gel column with chloroform eluent. The lower colored zone was separated, which, after evaporation of the solvent, yielded 2.5 g (56%) (V), mp 225-226°C [8].

CONCLUSIONS

1. Paramagnetic esters of benzenepolycarboxylic acids were synthesized and their ESR spectra were studied.

2. The spin exchange in the polyradicals obtained is stepwise in nature.

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PERFLUOROISOPROPYLIDENE AND PERFLUOROISOPROPENYL

DERIVATIVES OF PHOSPHORUS.

1. SYNTHESIS OF PERFLUOROISOPROPENYLPHOSPHONATES*

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In light of the high reactivity and variety of transformations of perfluorometacrylic acid derivatives [2], it was of interest to synthesize and study the properties of their "phosphorus analogs," namely, derivatives of pentafluoroisopropenylphosphonic acid.⁺ By analogy with the methods known for preparing perfluoromethacrylic acid derivatives [2], we might have expected the formation of esters of pentafluoroisopropenylphosphonic acid (I) by the dehydro-fluorination of esters of α -hydrohexafluoroisopropylphosphonic acid (II) or by the elimination of an alkyl fluoride from hexafluoroisopropylidenetrialkoxyphosphoranes (III).

*See [1] for previous communication. †The derivative of the isomeric pentafluoropropenylphosphonic acid CF₃CF=CFPO·(OEt)₂ was described previously [3].

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