EFFECT OF SUBSTITUENTS ON THE PARAMETER OF INTRAMOLECULAR EXCHANGE INTERACTION IN N,N'-DIOXY-2,6-DIAZAADAMANTANE BIRADICAL

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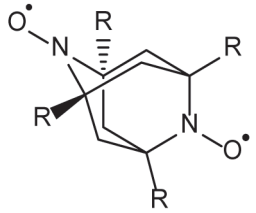
Density-functional calculations of a series of stable organic biradicals on the basis of a N,N'-dioxy-2,6-diazaadamantane core with different substituents have been performed using the UB3LYP/6-311++G(2d,2p) method. Using breaking symmetry approach[1], the values of the exchange interaction parameter, *J*, between the two spin centers are calculated. The chemical formulas of the studied organic biradicals are follows:



R= H, CH_3, C_2H_5, C_3H_7, i-C_3H_7, F, Cl, Br, CF_3, CCl_3, CBr_3, CH_2Cl, CH_2Br, $CH_2C_5H_6$, CH_2OH, OCH_3

It is shown that the intramolecular exchange interaction is mainly ferromagnetic in nature, but the *J* parameter gradually decreases, changing to antiferromagnetic interaction for the last four substituents, in the following sequence: CH_2OH > H > CBr_3 > CCl_3 > CH_3 > C_2H_5 > C_3H_7 > *i*-C_3H_7 > F > Br > > OCH_3 > Cl > CH_2Cl > CH_2Br > $CH_2C_5H_6$ > CF_3 (see table).

Table 1. *Values of the intramolecular exchange interaction parameter, J (cm^{-1}), for different R*

CH_2OH	H	CBr_3	CCl_3	CH_3	C_2H_5	C_3H_7	*i*-C_3H_7
14.19	11.87	11.65	9.26	6.56	5.22	4.43	4.39

F	Br	OCH_3	Cl	CH_2Cl	CH_2Br	$CH_2C_6H_5$	CF_3
1.45	1.34	0.33	0.13	–1.93	–2.35	–2.46	–7.33

It is concluded that the *J* parameter depends on the electron-donating/electron-withdrawing effects, geometry, and bulkiness of the substituents in the 1, 3, 5, and 7 positions of an adamantane core, and their specific interactions with the nitroxide radical groups.

References

1. Noodleman L., *J. Chem. Phys*. 1981, **74**, 5737.
2. Noodleman L., Baerends E. *J., J. Am. Chem. Soc*. 1984, **106**, 2316.