

Magnetic Properties of Acenes and Their *o*-Quinone Derivatives: Computer Simulation

A. A. Starikova^{a,*}, A. G. Starikov^a, R. M. Minyaev^a,
A. I. Boldyrev^{a,b}, and Academician V. I. Minkin^a

Received September 14, 2017

Abstract—Quantum chemical study (DFT UB3LYP/6-311++G(d,p)) of the structure and properties of acenes functionalized with two *o*-benzoquinone groups and their complexes with sodium cations has been performed. An increase in the number of fused rings has been shown to result in the stabilization of biradicaloid state of acenes and the switching of the character of exchange interactions between redox-active moieties from antiferromagnetic to ferromagnetic. The obtained results allow one to consider *o*-quinone acene derivatives as a basis for designing magnetoactive compounds.

DOI: 10.1134/S0012500818020015

Acenes **1** are the most widespread kind of fused aromatic polycyclic hydrocarbons, which are intensely studied for more than a century (Fig. 1). Doping the acene chain with electron-donating or electron-withdrawing atoms and organic or organometallic molecules allows one to vary the electronic structure of the system and provides a possibility to prepare materials with unusual electric and magnetic properties [1–3]. These polyaromatic compounds are considered as a basis for organic field-effect transistors [4] and organic semiconductors [5]. Considerable variation in the properties with a change in the number of fused rings is a specific feature of acenes. In particular, an increase in the length of oligomer molecule leads to a considerable decrease in the HOMO–LUMO energy gap, while compounds containing six and more rings are biradicals [6], this fact can be used in molecular electronics and spintronics [7].

Pentacene is the most studied member of this series. It shows semiconducting properties and is a promising candidate for application as an organic field-effect transistor (OFET). However, instability of this compound and its homologs—hexacene and heptacene—toward light and air makes difficult their practical application [8]. To solve this problem, it was suggested to use derivatives with paramagnetic substituents showing high stability on exposure to light due to

ultrafast singlet–triplet conversion of acene moiety in photoexcited states [9, 10].

The aim of this work is to study acenes **2** modified with two *o*-benzoquinone groups and their complexes with sodium cations **3** containing free-radical semiquinone (SQ) states of redox-active moieties (Fig. 2). The biradical state of acenes is expected to facilitate the appearance of supplementary exchange interactions between paramagnetic centers of complexes **3** whose character and strength may be governed by the polyacene chain length.

All computations were performed with the aid of the Gaussian 09 program [11] by the density functional theory (DFT) method using the UB3LYP functional, which correctly reproduces geometrical and magnetic characteristics of open-shell compounds [12], and the standard 6-311++G(*d,p*) basis set. Localization of stationary points on the potential energy surface (PES) was carried out by complete optimization of molecular structure geometry with computation of force constants and verification of the DFT wave function stability. Exchange interaction parameters (J , cm⁻¹) were calculated for all possible spin states of isomers within the broken symmetry (BS) formalism [13] with the use of the generalized spin projec-

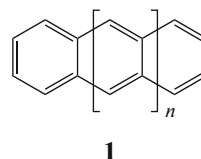


Fig. 1. General formula of acenes **1**.

^a Research Institute of Physical and Organic Chemistry, Southern Federal University, Rostov-on-Don, 344090 Russia

^b Department of Chemistry and Biochemistry, Utah State University, Old Main Hill, Logan, Utah, 84322, USA

*e-mail: alstar@ipoc.sfedu.ru; alstarchem@gmail.com

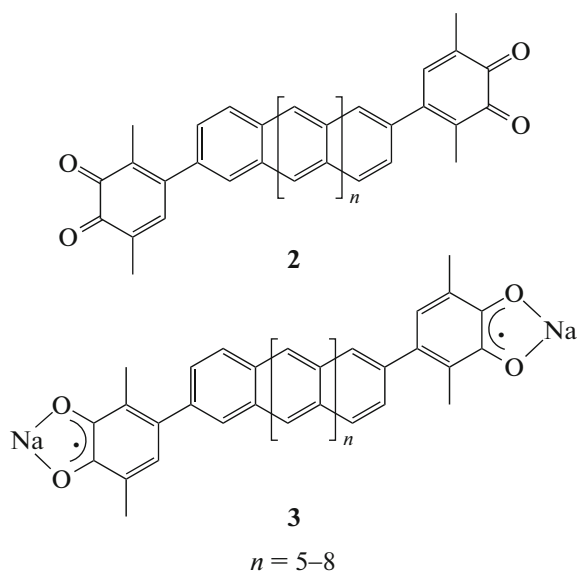


Fig. 2. General formula of acenes **2** and their sodium complexes **3**.

tion method suggested by Yamaguchi [14] and the Ruiz approach [15].

Figure 3 displays computation results for high-spin structures of heptacene ($n = 5$), di-*o*-benzoquinone derivative **2** ($n = 5$), and its complex with sodium cat-

Table 1. Spin (S), total energy (E_{total}), relative energy (ΔE), spin-squared operator S^2 , exchange interaction parameter ($J_{C_n-C_n}$) in compounds **1–2** ($n = 5–8$) calculated by DFT B3LYP/6-311++G(d,p)

Structure	S	E_{total} , au	ΔE , kcal/mol	S^2	$J_{C_n-C_n}$, cm^{-1}
1 ($n = 5$)	2/2	-1153.54126		2.027	-1562
BS	0	-1153.55161	6.5	0.573	
1 ($n = 6$)	2/2	-1307.99464		2.038	-1977
BS	0	-1308.00320	5.4	1.088	
1 ($n = 7$)	2/2	-1461.66614		2.041	-2075
BS	0	-1461.67369	4.7	1.243	
1 ($n = 8$)	2/2	-1615.33627		2.043	-2650
BS	0	-1615.34431	5.0	1.377	
2 ($n = 5$)	2/2	-2072.34181		2.036	-1869
BS	0	-2072.35272	6.8	0.755	
2 ($n = 6$)	2/2	-2226.01500		2.039	-1885
BS	0	-2226.02352	5.3	1.046	
2 ($n = 7$)	2/2	-2379.68640		2.041	-2087
BS	0	-2379.69401	4.8	1.241	
2 ($n = 8$)	2/2	-2533.35664		2.043	-2651
BS	0	-2533.36459	5.0	1.386	

Values of $J_{C_n-C_n}$ calculated using the formulas by Yamaguchi [14] and Ruiz [15] coincide.

ion **3** ($n = 5$). Compounds with $n = 6–8$ are not shown because they have a similar structure. Comparison of calculated geometrical characteristics of polyaromatic moieties of molecules **1–3** shows the lack of a considerable difference between them. Benzoquinone moieties in compounds **2** are turned relative to hydrocarbon chain plane by an angle of 49° . The spin density distribution shown in Fig. 3 indicates that this characteristic for acenes under consideration is independent of the presence of additional paramagnetic centers. The highest spin density is located at the opposite carbon atoms of central rings. According to computation results, the ground states of polyacenes **1** and **2** ($n = 5–8$) are singlet biradicals stabilized relative to the structures on the triplet PES by 4.7–6.8 kcal/mol. Optimization of closed-shell isomers leads to minima on the singlet PES characterized by unstable DFT wave function. Considerable antiferromagnetic exchange interactions between unpaired electrons delocalized at opposite carbon atoms are predicted, interaction strength increases with the number of annelated rings (Table 1). As it follows from calculated values of exchange interaction parameters, the value of this parameter on passing from heptacene ($n = 5$) to deca-cene ($n = 8$) changes from -1562 to -2650 cm^{-1} in acenes **1** and from -1869 to -2651 cm^{-1} in compounds **2**.

Complexes **3** with sodium cations stabilizing radical-containing forms of quinone moieties are characterized by the existence of three exchange channels J_{C_n-SQ} , J_{SQ-SQ} , and $J_{C_n-C_n}$ (Fig. 4).

With the aim to study the effect of acene biradicaloid state on exchange interactions between semiquinone fragments, we computed complexes with a lower number of annelated rings having closed electron shell. Computation for complexes **3** with phenylene linker and with anthracene ($n = 1$) and pentacene ($n = 3$) fragments showed that structures with paramagnetic hydrocarbon fragment are substantially destabilized. Therefore, exchange interactions in these compounds are possible only between unpaired electrons of the semiquinone moieties. The calculated exchange parameters point to the antiferromagnetic ordering in the complex with one aromatic ring ($J = -61 \text{ cm}^{-1}$); this parameter in anthracene and pentacene complexes is about -30 cm^{-1} .

In complexes of **3** ($n = 5–8$), like in unsubstituted molecules **1**, exchange interactions $J_{C_n-C_n}$ show a strong antiferromagnetic character and increase with the chain length (Table 2). Unpaired electrons of the redox-active moieties and polyaromatic system show antiferromagnetic interaction. On passing along a homologous series, acene–semiquinone exchange (J_{C_n-SQ}) attenuates due to an increase in the distance between the delocalized paramagnetic centers. In contrast to the above-considered closed-shell acenes, compounds **3** ($n = 5–8$) can exhibit ferromagnetic

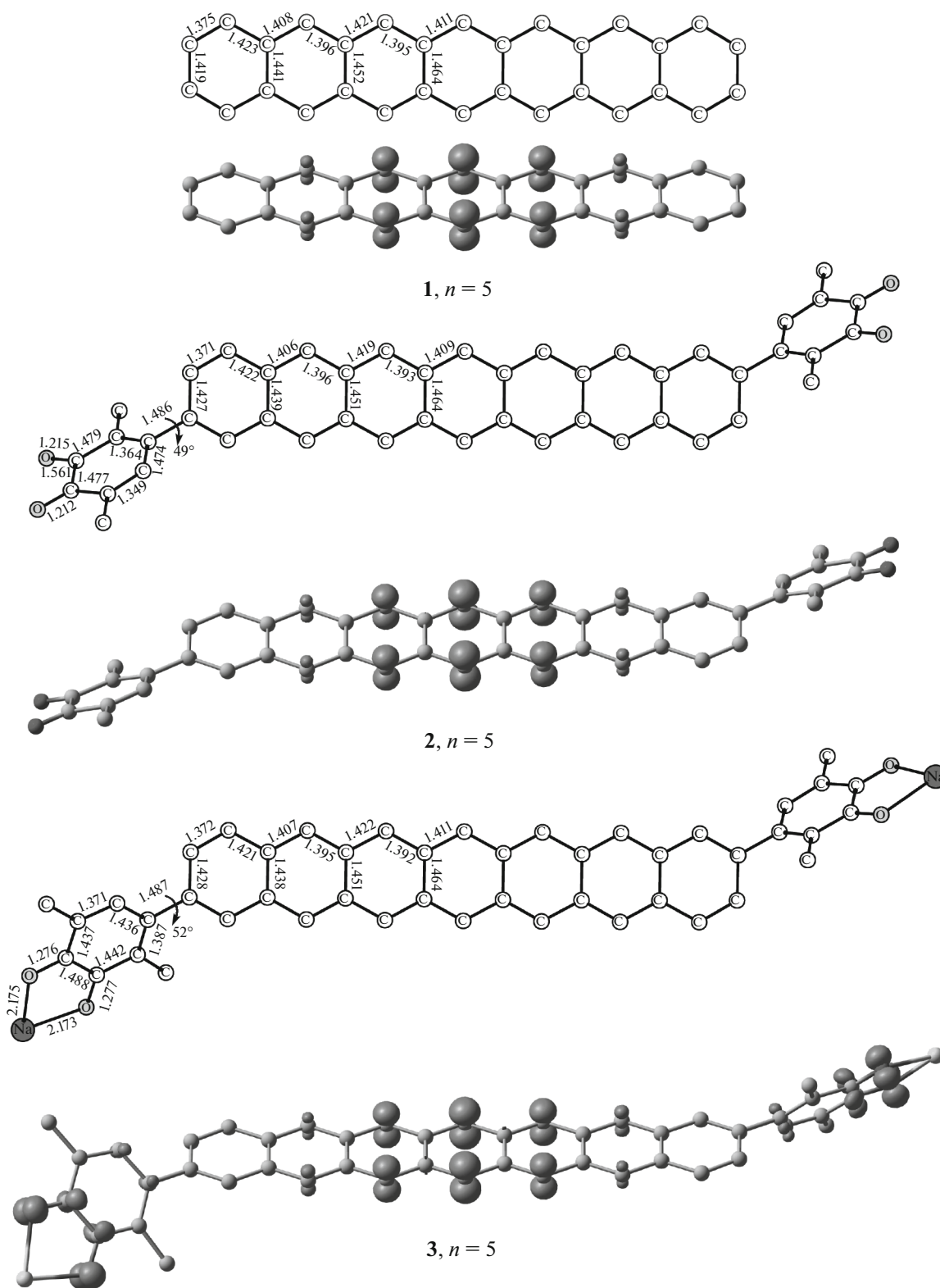


Fig. 3. Geometrical characteristics and spin density distribution in compounds 1–3 ($n = 5$) calculated by DFT UB3LYP/6-311++G(d,p). Bond distances and angles are given in Å and deg, respectively.

exchange between semiquinones (J_{SQ-SQ}). This fact allows one to draw a conclusion that acene biradical states switch exchange interaction character from anti-ferromagnetic to ferromagnetic.

Thus, the performed DFT UB3LYP/6-311++G(d,p) computer simulation showed that the insertion of *o*-benzoquinone groups into terminal acene rings imparts them supplementary functional-

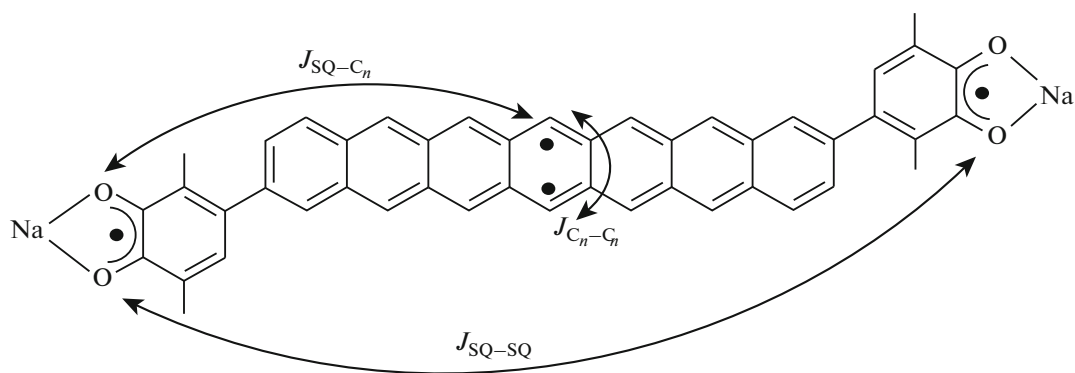


Fig. 4. Scheme of exchange interactions in complexes 3.

ity. The complexation of quinone moieties in compound 2 with metal cations leads to formation of additional paramagnetic centers, and exchange interactions between them can be governed by chain length.

This makes the considered quinone-containing acenes to be appropriate basis for constructing magnetoactive transition-metal binuclear coordination compounds.

Table 2. Spin (S), total energy (E_{total}), spin-squared operator S^2 , parameter of exchange interaction between opposite hydrocarbon chains ($J_{C_n-C_n}$), between acene fragment and semiquinone (J_{C_n-SQ}), between semiquinones (J_{SQ-SQ}) in complexes 3 ($n = 5-8$) calculated by B3LYP/6-311++G(d, p)

Structure	S	E_{total} , au	S^2	$J_{C_n-C_n}$, cm^{-1}	J_{C_n-SQ} , cm^{-1}	J_{SQ-SQ} , cm^{-1}
$n = 5$						
$\alpha\alpha\alpha\alpha$	4/2	-2397.12455	6.050	-1804	-71	114
$\alpha\beta\alpha\alpha = \alpha\alpha\beta\alpha$	2/2	-2397.13649	2.717	(-2362)	(-72)	(116)
$\beta\alpha\alpha\alpha = \alpha\alpha\alpha\beta$	2/2	-2397.12521	3.012			
$\alpha\alpha\beta\beta = \alpha\beta\alpha\beta$	0	-2397.13544	1.690			
$\alpha\beta\beta\alpha$	0	-2397.12586	1.977			
$n = 6$						
$\alpha\alpha\alpha\alpha$	4/2	-2550.79755	6.053	-1988	-51	115
$\alpha\beta\alpha\alpha = \alpha\alpha\beta\alpha$	2/2	-2550.80759	3.028	(-1988)	(-51)	(115)
$\beta\alpha\alpha\alpha = \alpha\alpha\alpha\beta$	2/2	-2550.79800	3.028			
$\alpha\alpha\beta\beta = \alpha\beta\alpha\beta$	0	-2550.80655	2.027			
$\alpha\beta\beta\alpha$	0	-2550.79849	2.001			
$n = 7$						
$\alpha\alpha\alpha\alpha$	4/2	-2704.46905	6.056	-1956	-38	108
$\alpha\beta\alpha\alpha = \alpha\alpha\beta\alpha$	2/2	-2704.47716	3.219	(-1598)	(-38)	(108)
$\beta\alpha\alpha\alpha = \alpha\alpha\alpha\beta$	2/2	-2704.46939	3.036			
$\alpha\alpha\beta\beta = \alpha\beta\alpha\beta$	0	-2704.47618	2.221			
$\alpha\beta\beta\alpha$	0	-2704.46974	2.018			
$n = 8$						
$\alpha\alpha\alpha\alpha$	4/2	-2858.13936	6.060	-2449	-28	105
$\alpha\beta\alpha\alpha = \alpha\alpha\beta\alpha$	2/2	-2858.14761	3.372	(-1653)	(-28)	(105)
$\beta\alpha\alpha\alpha = \alpha\alpha\alpha\beta$	2/2	-2858.13959	3.045			
$\alpha\alpha\beta\beta = \alpha\beta\alpha\beta$	0	-2858.14667	2.367			
$\alpha\beta\beta\alpha$	0	-2858.13988	2.030			

Exchange interaction parameters were calculated using Yamaguchi's formula [14]. Values in parentheses were calculated using the Ruiz approach [15]. α corresponds to the upward spin orientation, and β corresponds to the downward spin orientation.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Education and Science of the Russian Federation (grant for Leading Scientists no. 14.Y26.31.0016).

REFERENCES

1. Dimitrakopoulos, C.D. and Malenfant, P.R.L., *Adv. Mater.*, 2002, vol. 14, no. 2, pp. 99–117.
2. Bromley, S.T., Mas-Torrent, M., Hadley, P., and Rovira, C., *J. Am. Chem. Soc.*, 2004, vol. 126, no. 21, pp. 6544–6545.
3. Starikov, A.G., Minyaev, R.M., and Minkin, V.I., *Dokl. Chem.*, 2006, vol. 409, no. 2, pp. 113–116.
4. Anthony, J.E., *Angew. Chem., Int. Ed. Engl.*, 2008, vol. 47, no. 3, pp. 452–483.
5. Bredas, J.-L., Beljonne, D., Coropceanu, V., and Cornil, J., *Chem. Rev.*, 2004, vol. 104, no. 11, pp. 4971–5004.
6. Bendikov, M., Duong, H.M., Starkey, K., Houk, K.N., Carter, E.A., and Wudl, F., *J. Am. Chem. Soc.*, 2004, vol. 126, no. 24, pp. 7416–7417.
7. Castellano, M., Ruiz-Garcia, R., Cano, J., Ferrando-Soria, J., Pardo, E., Fortea-Perez, F.R., Stiriba, S.-E., Barros, W.P., Stumpf, H.O., Canadillas-Delgado, L., Pasan, J., Ruiz-Perez, C., de Munno, G., Armentano, D., Journaux, Y., Lloret, F., and Julve, M., *Coord. Chem. Rev.*, 2015, vol. 303, pp. 110–138.
8. Kawanaka, Y., Shimizu, A., Shinada, T., Tanaka, R., and Teki, Y., *Angew. Chem., Int. Ed. Engl.*, 2013, vol. 52, no. 26, pp. 6643–6647.
9. Kanemoto, K., Fukunaga, A., Yasui, M., Kosumi, D., Hashimoto, H., Tamekuni, H., Kawahara, Y., Takemoto, Y., Takeuchi, J., Miura, Y., and Teki, Y., *RSC Adv.*, 2012, vol. 2, no. 12, pp. 5150–5153.
10. Katayama, K., Hirotsu, M., Kinoshita, I., and Teki, Y., *Dalton Trans.*, 2014, vol. 43, pp. 13384–13391.
11. Frisch, M.J., Trucks, G.W., Schlegel, H.B., et al., Gaussian-09, Rev. D.01, Gaussian, Inc., Wallingford, 2013.
12. Starikova, A.A., Starikov, A.G., and Minkin, V.I., *Russ. J. Coord. Chem.*, 2015, vol. 41, no. 8, pp. 487–495.
13. Noodleman, L., *J. Chem. Phys.*, 1981, vol. 74, no. 10, pp. 5737–5743.
14. Shoji, M., Koizumi, K., Kitagawa, Y., Kawakami, T., Yamanaka, S., Okumura, M., and Yamaguchi, K., *Chem. Phys. Lett.*, 2006, vol. 432, no. 1, pp. 343–347.
15. Ruiz, E., in *Comprehensive Inorganic Chemistry II*, Ed. by Reedijk, K. and Poeppelmeier, K., Elsevier, 2013, vol. 9.

Translated by I. Kudryavtsev