

Electronic Structure of Dodecyl Syringate Radical Suitable for ESR Molecular Quantum Computers

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Abstract. The neutral radical of dodecyl syringate is suggested as a candidate for molecular Electron Spin Resonance (ESR) quantum computers. The first principle of quantum chemical calculations indicates that this molecule with a stable delocalised electron spin may represent a qubit in quantum information processing. The spin density analysis exhibits that unpaired spin of the radical is delocalised in the region of not-compensated valence bond. Isotropic Fermi contact coupling constants and anisotropic spin dipole couplings was investigated and indicated the largest hyperfine splitting (HFS) of ESR spectra on atoms of the above mentioned region of not-compensated valence bond.

Keywords: quantum bits, quantum computers, logic gates, radical, syringate.

1 Introduction

A quantum computer is a machine that performs information processing based on principles of quantum mechanics. Recent progress in the algorithm applying for quantum calculation has spurred the implementation of the quantum computers in actual physical systems. The main challenge on the way to a universal quantum computer is to achieve control over single quantum mechanical two state system while preserving long decoherence times [1].

Electron and nuclear spins have been identified as promising candidates for qubits because they are natural two state systems and decoherence times for the spin degree of freedom are unusually large. The variety of molecules with their widespread properties to offer bright interesting field for investigations concerning elements of quantum computation. Among other systems proposed so far, the molecular nano-devices should be one of the most promising candidates, because of the possibility to isolate them from the environment and good controllability with the well-established technique of electron spin resonance (ESR). On the other hand, the molecular device should be logically controlled by light and that could be applied for quantum computation also [2, 3].

During the last decade important works have been done towards molecular electronics. D. Kuciauskas *et al.* constructed molecule-scale AND logic gate based on fullerene containing charge transfer triads [4]. G. Leatherman *et al.* [5] and K.A. Jolliffe *et al.* [6] have done series of experiments with charge separation in photoexcited electron donor-acceptor molecular wires. Recently important research in the field of computing with molecules was done by M.A. Reed and Z.J. Donhauser *et al.* [7, 8]. Artificial light-fueled molecular-level abacus and machines, switches, plug/socket systems based on interlocked molecular compounds are constructed by N. Armaroli, P.R. Ashton, V. and Y. Luo *et al.* [9]–[11]. Light-driven monodirectional molecular rotors are recently synthesized by N. Koumura *et al.* [12].

Detailed experimental studies, establishing the surface-initiated mechanism for the photoinduced relief grating formation on azo-benzene functionalized polymer films were performed by C.J. Barrett *et al.* [13], J. Kumar *et al.* [14] and P. Lefin *et al.* [15]. Moreover, some molecules indicate perfect magnetic properties. Recently, broad NMR spectra of the Cu octaethylbilindione (CuOEB), CoOEB, ZnOEBOMe, Mn octaethylbilindione dimmer (Mn2OEB) and Fe2OEBOMe are experimentally observed [16]–[19].

Through combined synthetic, analytic, and spectroscopic work, a five-bit NMR quantum computer was built and shown to implement superposition, quantum interference, and designed unitary transformations. IBM chemists designed and made a new molecule that has seven nuclear spins which can interact with each other as qubits, be programmed by radio frequency pulses

and be detected by nuclear magnetic resonance (NMR) instruments similar to those commonly used in hospitals and chemistry labs. Scientists at MIT and Los Alamos National Laboratory created a seven-qubit quantum computer within a single drop of liquid [20, 21].

Synthesis and investigations of novel stable organic radicals are important for the development of spin chemistry underlying molecular-based magnetic materials [22]. Mono radical systems showing a remarkably topology-dependent spin diversity nature appearing in a series of oxophenalenoxyl system, as well as two kinds of naphthoxyl radicals in term of the spin-density distributions. Hyperfine splitting was obtained due to protons of radicals by solution ESR/ENDOR, and indicate unpaired electron delocalization. Thus, the radicals seem to be good candidate to generate qubits. Recently, the conformation-dependent quantum optical behavior of the polymeric molecules has been observed and proposed that the controlled tuning of the number of active sites could be found applications as a source for single or few photons in quantum cryptography quantum computing and data storage.

As was mentioned above, in the quantum computation the molecules with nuclear or electron spins is programmed by radio frequency pulses and detected with NMR or EPR technique. However, new approach which makes use of optimal control theory for vibration excitations in molecular system is presented [23]. Several works indicate that photo excitation should be controlled also. Thus, the question arises do it is possible to adopt well known properties of molecular devices to the quantum computation. Following this line of thought, we intend to investigate molecule that optical properties could be applied for quantum calculation (Fig. 1). Roughly speaking, our aim is to show the principle possibility for the combination of the photo excitation and quantum computing and to bring up a new conceptual idea without claiming to solve all problems of quantum computation. In this paper we suggested and investigated the neutral radical of dodecyl syringate and exhibit possibility to use photo-excitation (instead electromagnetic field) to perform quantum-computations. This radical shows two remarkable features, i.e. it is rather stable among organic radicals [24]; it contains hydrophobic tail that can be used for self assembled mono layers [25] formation.

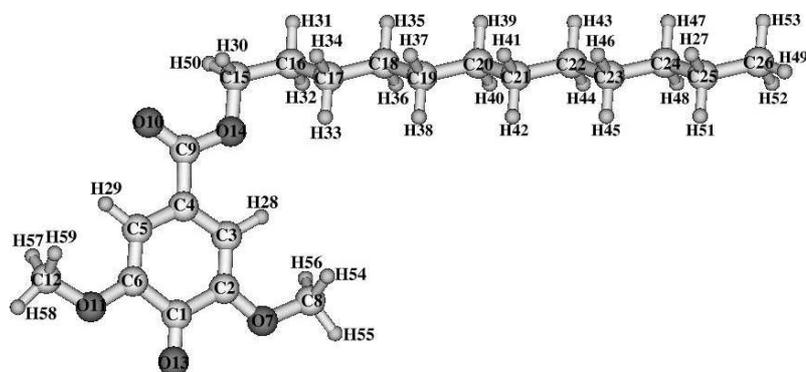


Fig. 1. Geometry of optimized dodecyl syringate radical.

2 Method of investigations

The two key tasks for quantum-logic operations are: the first to find a physical system of quantum bits and second, to design the quantum logic gates. In an effort to shed light on the subject, computations of dodecyl syringate radical were performed to support an idea to accept obtained properties for quantum computing because this molecule bears a marked resemblance to polymer ones, that usually exhibit electro- and photoluminescent properties. The geometry search of this radical was performed applying UB3LYP method with 6-311G** basis set within Becke optimization [26]. Currently, the above model is considered to be the most appropriate model to take into consideration electron correlations in large open-shell neutral radical molecules [27, 28]. It should be emphasized, that we intend to find derivative suitable to perform EPR quantum computation. Thus, the investigation of hyperfine coupling and spin density should be performed. The studies of hyperfine coupling and other molecular properties in organic radicals performed by V. Barone indicated that the sufficient accuracy of isotropic hyperfine coupling constants evaluation using unrestricted DFT with hybrid B3LYP exchange-correlation functional can be achieved using the re-optimized by atomic calculations Huzinaga-Dunning double-zeta basis sets augmented with additional polarization functions and uncontracted in outer core – inner valence region, so called EPR-II basis functions [29]. Thus, the geometry obtained by the optimization was used to perform the single point calculations of the properties of neutral radical molecules

applying EPR-II basis set. In all calculations the Gaussian 98 program was used [30].

3 Results of investigations

The obtained geometry structure of our investigated neutral radical is shown in Fig. 1 and Table 1.

Table 1. The main distances and angles of the dodecyl syringate radical obtained after full geometry optimization

Bond	Distance, $\overset{\circ}{\text{A}}$	Bonds	Angle, degrees
C1-C2	1.48	C1-C2-C3	121.58
C1-O13	1.23	C2-C3-C4	119.71
C1-C6	1.48	C3-C4-C5	121.83
C2-C3	1.38	C4-C5-C6	120.01
C2-O7	1.34	C5-C6-C1	121.38
C3-C4	1.41	C2-O7-C8	118.67
C4-C5	1.41	C6-O11-C12	118.55
C4-C9	1.38	C3-C4-C9	121.5
C5-C6	1.38	C9-O14-C15	116.18
C6-O11	1.34	O10-C9-O14	123.24
C7-C8	1.42	O13-C1-C2	122.18
C9-O10	1.21	O14-C15-C16	108.09
C9-O14	1.35		
C11-C12	1.43		
C15-C16	1.52		

The comparison of the bonds lengths indicate shorter single C-O bond between C2-O7, C6-O11, C9-O14 than that of C8-O7, C12-O11, C15-O14. Moreover, the values of overlap population of the shortest C-O bonds are approximately twice larger than that of longer ones. These results indicate that “free electron” localize on the C2-O7, C6-O11, C9-O14 bonds.

Theoretical values for the hyperfine interaction parameters of all the nuclei of the phenyl ring with the unpaired spin have been obtained for the ground and excited states using the UHF/EPR-II approach. To verify the reliability of the method in our particular case, the predicted interaction parameters have been compared with those experimentally obtained. Hyperfine coupling constant for the interaction with the spin radical have been reported in [31]. The parameters

obtained from theoretical calculations of the ground state of dodecyl syringate radical have been compared with those of other radicals. The parameters agree well that verify the reliability of the method. The data indicate very weak coupling in the ground state for H31, H32 and others atoms that is not presented in Table 2, and very strong constant hyperfine coupling for H28, H29. As shown in Table 2, the coupling constant should become very strong during excitation. As example of the above mentioned coupling constant increasing: the H56 atoms coupling constant is equal to 2.68 Mhz, while that in V excited state is of 12.21 Mhz, that indicate the strong coupling of H atoms that could be related with spin delocalization.

Table 2. Isotropic Fermi contact couplings (MHz) of dodecyl syringate radical in the ground and excited state calculated by UHF/EPR-II model

Atom	Ground state	I-st excited state	II-nd excited state	III-rd excited state	IV-th excited state	V-th excited state
H28	39.75	67.22	40.14	-78.09	72	40.11
H29	39.83	67.3	-6.28	-32.45	68.98	32.5
H30	0.84	1.12	2.22	-0.13	-6.06	2
H31	0.02	-0.15	-0.36	-0.05	5.67	-0.25
H32	-0.05	-0.09	0.01	0.07	1.42	-0.11
H54	2.68	2.87	4.17	1.91	3.69	12.23
H55	-1.05	-0.78	-0.47	-0.03	-0.9	-0.15
H56	2.68	2.88	4.16	1.91	3.68	12.21
H57	2.69	2.94	3.04	3.34	3.64	11.94
H58	-1.04	-0.73	-0.69	0.36	-0.89	-0.11
H59	2.7	3.05	3.03	3.34	3.69	11.72

The calculated spin density distribution in the ground state of dodecyl syringate radical is depicted in Fig. 2, showing polarization nature and unique tendency of spin density delocalization in the system; the unpaired electron is dominantly delocalised on the one oxygen atoms and on the five carbon of phenyl ring.

Our calculations reveal the complicated of the non-localized spin density (Table 3) due to the electron correlation forces between spins oriented to the same direction. This leads to the appearance of significant values of spin-down densities on the C1, C3 and C5 atoms.

The most interesting phenomena were obtained when atomic spin densi-

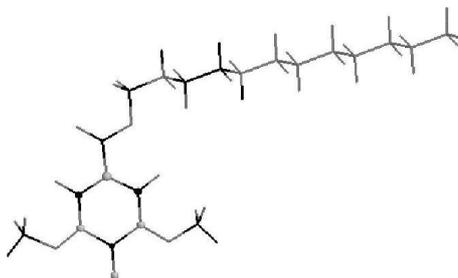


Fig. 2. The spin density distribution in the ground state of dodecyl syringate. The white and dark circles indicate α and β spins respectively.

Table 3. Total atomic spin densities of dodecyl syringate radical calculated by UB3LYP/EPR-II model in the ground and excited states

Atom	Ground state	I-st excited state	II-nd excited state	III-rd excited state	IV-th excited state	V-th excited state
C1	-0.513	-1.140	-0.278	-0.138	-0.463	1.809
C2	0.625	0.680	0.400	0.024	0.598	0.280
C3	-0.612	-0.573	-0.398	0.713	-0.649	-0.454
C4	0.696	0.584	0.274	-0.203	0.811	0.670
C5	-0.606	-0.568	0.019	0.271	-0.649	-0.379
C6	0.618	0.677	0.387	0.023	0.581	0.216
O7	0.033	-0.001	0.031	0.059	0.028	0.102
C8	-0.005	-0.001	-0.004	-0.011	-0.004	-0.017
C9	-0.136	-0.099	-0.173	0.065	-1.822	-0.123
O10	0.141	0.110	0.092	-0.105	1.854	0.113
O11	0.034	0.001	0.045	0.055	0.025	0.094
C12	-0.005	-0.001	-0.008	-0.008	-0.003	-0.016
O13	0.621	1.216	0.471	0.303	0.562	-1.391
O14	-0.003	0.004	0.106	0.027	0.022	0.017

ties were investigated in various excited state. It is possible to see (Table 3) that during excitation the spin density and direction are changed. For an example, the spin density of C3 atoms is equal to -0.470 in the ground state, while that in the III excited states becomes positive and equal to 0.713. Without any doubt this spin density changeability is related with charge transfer during excitation, because the negative charge of the C3 atom in the III excited state is smaller than that in the ground (see Table 4). Moreover, it is possible to see that several atoms spin direction are related: when C3 atom spin is down oriented the C4 and C10 atoms possess spin-up, while the spins orientation of these atoms is

down in the case of C3 spin-up.

Table 4. The point charge on the atoms of dodecyl syringate radical calculated by UB3LYP/EPR-II model in the ground and excited states

Atom	Ground state	I-st excited state	II-nd excited state	III-rd excited state	IV-th excited state	V-th excited state
C1	0.076	-0.080	0.081	0.126	0.083	0.489
C2	0.351	0.358	0.331	0.311	0.337	0.291
C3	-0.326	-0.329	-0.343	-0.187	-0.348	-0.294
C4	0.289	0.258	0.293	0.134	0.397	0.292
C5	-0.278	-0.278	-0.225	-0.184	-0.276	-0.250
C6	0.332	0.340	0.318	0.280	0.290	0.270
O7	-0.357	-0.395	-0.355	-0.317	-0.361	-0.305
C8	-0.145	-0.143	-0.143	-0.151	-0.143	-0.147
C9	0.278	0.283	-0.100	0.185	-0.089	0.255
O10	-0.376	-0.395	0.121	-0.263	0.110	-0.345
O11	-0.352	-0.390	-0.334	-0.318	-0.358	-0.301
C12	-0.143	-0.143	-0.147	-0.146	-0.142	-0.145
O13	-0.230	0.048	-0.304	-0.369	-0.263	-0.749
O14	-0.354	-0.355	-0.322	-0.359	-0.338	-0.350

The bottom line of the manuscript shows, that quantum computer design could be based on the combination of both EPR sequence measurement and excitation by light. The simple NOT gates could be designed applying as input and output the orientation of the spin of C3 and C4 atoms. In the ground state the spin density of C3 atoms is negative and equal to -0.470, while that of C4 is of 0.588. It means that if input is 1 the output will be 0. However, in the III excited state, the spin density of this C3 atom is equal to 0.713 (positive), while that of C4 atoms is negative (-0.201). Thus, if input is 0, the output will be 1. The simplest prediction indicates that it is possible to use photo-excitation (instead electromagnetic field) to perform quantum-computations.

4 Conclusions

It was previously mentioned that synthesis and investigation of novel stable organic radicals is important for the development of spin chemistry underlying molecular-based magnetic materials. The results of our investigations indicate

that dodecyl syringate radical possesses “free” electron that is localized on the three C-O bonds. The isotropic HFSs of this molecule is small, not-compensated spin in the ground state is delocalised on three carbon atoms of phenyl ring and one neighboring oxygen. Thus, this molecule could be applied as ESR molecular quantum computers. However, the spin delocalization on four atoms might cause some experimental problems constructing logic gates.

It is emphasize that obtained optical properties of this molecule could be applied for quantum calculation. The results of our investigations indicate spin flip in the excited state that allows us to combine the photo excitation and quantum computing and to bring up a new conceptual idea.

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