AM1 CALCULATIONS OF SPIN DISTRIBUTION IN HYDROXYANTHRASEMIQUINONES

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The AM1 method was used to obtain the optimum geometries of hydroxyanthrasemiquinones. The relation between the spin distribution data obtained by analysis of EPR spectra and by AM1 calculations depends on the position of the C atom within the aromatic skeleton, on its spin density sign and on its position relative to OH substituents. Complete annihilation of higher spin state contaminations is insufficient to eliminate the significant discrepancies between the theoretical and experimental data.

Anthraquinones[1] comprise the largest group of quinone pigments found in nature. Nearly all of them are polyhydroxy or alkoxy derivatives, and knowledge of how the unpaired electron spin density distributions are influenced by these substituents is of theoretical as well as practical interest.

Much of the insufficient insight into the electronic structure of radicals is due to drawbacks of the use of the Hartree–Fock wave functions[2]. For open-shell systems, the exact eigenfunctions are required to be eigenfunctions of both the square of the total spin-angular momentum $\langle \hat{S}^2 \rangle$ operator and of the z component of the $\hat{S}$ operator. While the restricted open-shell Hartree–Fock (ROHF) method satisfied these conditions, in the ROHF wave functions the spin polarization is neglected. The unrestricted Hartree–Fock (UHF) solution, on the other hand, accounts qualitatively for spin polarization but the wave function is no eigenfunction of the $\langle \hat{S}^2 \rangle$ operator (but it is an eigenfunction of $\langle \hat{S}_z \rangle$). Because of this, UHF wave functions contain contaminations by higher spin multiplets. A dominant part of the spin contaminations is due to contribution from the next higher spin state and can be annihilated via a projection technique[3].

In the following, spin annihilation will refer to the removal of the major spin contamination due to the next higher spin state of the UHF wave function, and the wave function thus produced will be referred to as the projected unrestricted Hartree–Fock (PUHF) wave function. UHF functions after complete annihilation of all spin contaminants will be denoted as CPUHF. “Spin delocalization” and “spin polarization” have been used to classify “spin appearing” mechanisms[4–6] that are due to singly occupied orbitals of the best restricted wave functions or due to correlation between electron spins, respectively. This allows for the separation of the spin density calculated by using the UHF method without and with annihilation into components due to the spin polarization mechanism (SPM) and the spin delocalization mechanism.

The SPM contributions to the spin densities ρ associated with the various stages of annihilation satisfy the relation

$$\rho^{SPM}\,(\mathrm{UHF}) : \rho^{SPM}\,(\mathrm{PUHF}) : \rho^{SPM}(\mathrm{CPUHF}) = (s+2) : (s+1) : s\ , \qquad (1)$$

where the spin density function ρ is the difference between the α and β electron density and s is the spin operator eigenvalue. Consequently, the ratio between the integrated spin populations N (i.e. the difference between the α and β electron populations) determined at the UHF and PUHF levels may also be a constant[1].

It is found that while the electron populations determined at the UHF and PUHF levels differ only marginally, the spin populations N are greatly dependent on the level used[2,7,8]. The spin population ratios N(UHF)/N(PUFH) calculated at the *ab initio* level for the C atoms in the σ radicals are always found to be about 1.1 whereas in the π systems the ratios span a large range[2] from 1.2 to 1.6. For atoms with excess of α spin in the UHF densities, the spin annihilation increases the β spins and decreases the α spins by about the same amount and vice versa. For heavily spin contamined systems such as π radicals the spin population diffrence $\Delta N = N(\mathrm{PUHF}) - N(\mathrm{UHF})$ attains values as large as 0.25–0.4.

Quantum-chemical calculations of EPR spectra are usually based on a proportionality between the coupling constants and the UHF spin population of the relevant hydrogen atom, using an empirical proportionality constant[9]. Failure of this treatment for aromatic and other π electron systems is ascribed to a too high spin contamination (even after quartet annihilation) and/or to an improper geometry of the systems under study[9,10]. The aim of this study is to find the relation between the calculated and experimentally observed spin distribution on the anthraquinone skeleton for a series of hydroxyanthrasemiquinones.

CALCULATIONS

The standard semiempirical AM1 method of quantum chemistry (AMPAC program package)[11,12] was used in order to find the optimal geometries and to calculate the electronic structures of selected hydroxyanthrasemiquinones (see Table I). All calculations were performed in higher precision (keyword PRECISE) using the Davidon–Fletcher–Powell optimization procedure[13,14]. The calculated spin populations N at the ROHF and UHF levels for relevant carbon atoms are compared with the experimental spin populations at carbon atoms derived from the coupling constants for hydrogen atoms a_H using McConnel's relation[15] (i.e. proportionality of a_H to the π electron spin population at the carbon atom of the aromatic skeleton).

RESULTS AND DISCUSSION

The hydrogen coupling constants[1] a_H for the systems presented in Table I are compared with the spin populations N calculated at the ROHF, UHF and PUHF levels of the AM1 method for relevant C atoms in Table II (the a_H values for the B27 and B2367 systems were not measured but calculated by the additivity principle). It is evident that the spin population ratio $K = N(\text{UHF})/N(\text{PUHF})$ is constant for each of the systems. This fact implies the possibility of obtaining this ratio[2,4–6] at the CPUHF level by extrapolation for $N(\text{PUHF}) = 0.75$ based on Eq. (*1*). Approximation of the population ratio K for the

TABLE I
Systems studied and their symbols

Symbol	Compound
	α-Hydroxyanthrasemiquinones
A1	1-hydroxy-9,10-anthrasemiquinone
A14	1,4-dihydroxy-9,10-anthrasemiquinone
A15	1,5-dihydroxy-9,10-anthrasemiquinone
A18	1,8-dihydroxy-9,10-anthrasemiquinone
A145	1,4,8-trihydroxy-9,10-anthrasemiquinone
A1458	1,4,5,8-tetrahydroxy-9,10-anthrasemiquinone
	β-Hydroxyanthrasemiquinones
B2	2-hydroxy-9,10-anthrasemiquinone
B23	2,3-dihydroxy-9,10-anthrasemiquinone
B26	2,6-dihydroxy-9,10-anthrasemiquinone
B27	2,7-dihydroxy-9,10-anthrasemiquinone
B2367	2,3,6,7-tetrahydroxy-9,10-anthrasemiquinone
	α,β-Hydroxyanthrasemiquinones
C1256	1,2,5,6-tetrahydroxy-9,10-anthrasemiquinone
C1258	1,2,5,8-tetrahydroxy-9,10-anthrasemiquinone
C1368	1,3,6,8-tetrahydroxy-9,10-anthrasemiquinone

TABLE II
Observed coupling constants[a] a_H, calculated spin populations N at the ROHF, UHF and PUHF levels, and their ratio $K = N$(UHF)/N(PUHF) for relevant positions n in the systems studied

System	n	a_H, 10^{-4} T	N			K
			ROHF	UHF	PUHF	
A1	2	1.57	0.05087	–0.01644	–0.00399	4.120
	3	1.17	0.05476	0.02096	0.00509	4.118
	4	1.04	0.01446	–0.02136	–0.00519	4.116
	5	0.50	0.00983	–0.01786	–0.00434	4.115
	6	0.86	0.05033	0.01804	0.00438	4.119
	7	1.09	0.04558	–0.01322	–0.00321	4.118
	8	0.65	0.01285	0.01353	0.00328	4.125
A14	2	2.13	0.06133	0.02281	0.00563	4.052
	3	2.13	0.06101	–0.01652	–0.00408	4.049
	5	0.53	0.01136	0.01136	0.00280	4.057
	6	0.91	0.04372	–0.01096	–0.00270	4.059
	7	0.91	0.04392	0.01560	0.00385	4.052
	8	0.53	0.01125	–0.01543	–0.00381	4.050
A15	2	1.71	0.05098	0.01672	0.00446	3.749
	3	1.35	0.04959	–0.01049	–0.00280	3.746
	4	0.94	0.01692	0.01139	0.00304	3.747
	6	1.71	0.05218	–0.01264	–0.00337	3.751
	7	1.35	0.05116	0.01773	0.00473	3.748
	8	0.94	0.01706	–0.01824	–0.00487	3.745
A18	2	1.68	0.04699	–0.01922	–0.00376	5.112
	3	1.27	0.05378	0.02270	0.00444	5.113
	4	0.92	0.01396	–0.02305	–0.00451	5.111
	5	0.92	0.01458	–0.02336	–0.00457	5.112
	6	1.27	0.05540	0.02265	0.00443	5.113
	7	1.68	0.04858	–0.01871	–0.00366	5.112
A145	2	1.97	0.06077	0.02491	0.00480	5.190
	3	2.06	0.05720	–0.01975	–0.00380	5.197
	6	1.64	0.04706	–0.01776	–0.00342	5.193
	7	1.30	0.04962	0.02154	0.00415	5.190
	8	0.85	0.01618	–0.02217	–0.00427	5.192
A1458	2	1.85	0.05474	–0.01867	–0.00360	5.186
	3	1.85	0.05483	0.02390	0.00461	5.184
	6	1.85	0.05678	0.02358	0.00454	5.194
	7	1.85	0.05700	–0.01800	–0.00347	5.187

TABLE II
(*Continued*)

System	*n*	a_H, 10^{-4} T	*N*			*K*
			ROHF	UHF	PUHF	
B2	1	1.61	0.01772	0.01447	0.00389	3.720
	3	0.54	0.04588	0.01669	0.00449	3.717
	4	0.27	0.00686	–0.01651	–0.00444	3.718
	5	0.15	0.00946	–0.01652	–0.00444	3.721
	6	1.03	0.05262	0.01672	0.00450	3.716
	7	0.62	0.04768	–0.01144	–0.00308	3.714
	8	1.96	0.01253	0.01152	0.00310	3.716
B23	1	1.34	0.01258	–0.02108	–0.00524	4.023
	4	1.34	0.01309	0.01884	0.00468	4.026
	5	1.14	0.01118	0.01068	0.00265	4.030
	6	0.61	0.04969	–0.01058	–0.00263	4.023
	7	0.61	0.05003	0.01603	0.00398	4.028
	8	1.14	0.01098	–0.01589	–0.00395	4.023
B26	1	0.92	0.01600	–0.01875	–0.00493	3.803
	3	0.00	0.04293	–0.01468	–0.00386	3.803
	4	1.60	0.00834	0.01398	0.00367	3.809
	5	0.92	0.01684	0.01263	0.00332	3.804
	7	0.00	0.04488	0.01534	0.00403	3.806
	8	1.60	0.00855	–0.01546	–0.00406	3.808
B27	1	0.76	0.01958	0.01706	0.00423	4.033
	3	2.60	0.04753	0.01875	0.00465	4.032
	4	1.74	0.00577	–0.01834	–0.00455	4.031
	5	1.74	0.00602	–0.01840	–0.00456	4.035
	6	2.60	0.04982	0.01865	0.00463	4.028
	8	0.76	0.02076	0.01669	0.00414	4.031
B2367	1	1.97	0.01310	–0.02242	–0.00451	4.971
	4	1.97	0.01347	0.02054	0.00413	4.973
	5	1.97	0.01393	0.01998	0.00402	4.970
	8	1.97	0.01377	–0.02215	–0.00446	4.966
C1256	3	0.30	0.04387	–0.01897	–0.00378	5.019
	4	1.96	0.1371	0.01881	0.00375	5.016
	7	0.30	0.04539	0.02085	0.00416	5.012
	8	1.96	0.01417	–0.02208	–0.00440	5.018
C1258	3	1.72	0.04567	0.02341	0.00384	6.096
	4	1.71	0.01233	–0.02435	–0.00399	6.103
	6	2.46	0.06007	0.02556	0.00419	6.100
	7	0.38	0.05356	–0.02034	–0.00333	6.108

TABLE II
(*Continued*)

System	n	a_H, 10^{-4} T	N			K
			ROHF	UHF	PUHF	
C1368	2	3.30	0.04083	–0.02027	–0.00371	5.464
	4	1.15	0.02255	–0.02332	–0.00427	5.461
	5	1.15	0.02309	–0.02404	–0.00440	5.464
	7	3.30	0.04494	–0.01936	–0.00354	5.469

[a] Ref.[1].

TABLE III
Eigenvalues of the $\langle\hat{S}^2\rangle$ operator at the UHF and PUHF levels, spin population ratio K_{calc} = N(UHF)/N(PUHF) calculated based on Eq. (*2*) with relative deviations $\delta = 100\ (K_{calc} - K)/K$, and this ratio $K(0.75)$ extrapolated for $\langle\hat{S}^2(\text{PUHF})\rangle = 0.75$

System	$\langle\hat{S}^2\rangle$		K_{calc}	δ	$K(0.75)$
	UHF	PUHF			
A1	1.1099	0.8943	4.113	–0.13	4.388
A14	1.0958	0.8765	4.059	0.15	4.322
A15	1.0233	0.8285	3.751	0.10	3.984
A18	1.2654	1.0742	5.114	0.05	5.112
A145	1.2743	1.0822	5.192	–0.00	5.153
A1458	1.2742	1.0795	5.191	0.06	5.153
B2	1.0146	0.8238	3.717	–0.02	3.943
B23	1.0900	0.8748	4.027	0.04	4.295
B26	1.0375	0.8381	3.804	–0.04	4.050
B27	1.0916	1.8795	4.027	–0.13	4.302
B2367	1.2479	1.0496	4.968	–0.04	5.030
C1256	1.2533	1.0523	5.013	–0.06	5.055
C1258	1.3600	1.2173	6.099	–0.05	5.552
C1368	1.3032	1.1318	5.468	0.08	5.288

series of model systems in Table III by a polynomial function of the square of the total-spin angular $\langle \hat{S}^2 \rangle$ operator eigenvalues at the UHF and PUHF levels,

$$K = A_1 \langle \hat{S}^2(\mathrm{UHF}) \rangle + A_2 \langle \hat{S}^2(\mathrm{PUHF}) \rangle + A_{12} \langle \hat{S}^2(\mathrm{UHF}) \rangle \langle \hat{S}^2(\mathrm{PUHF}) \rangle + B \qquad (2)$$

was successful, as indicated by the statistical parameters presented in Table IV for various levels of parametrization. The spin population ratio $K(0.75)$ calculated by Eq. (*2*) for data in the last row of Table IV and for $\langle \hat{S}^2(\mathrm{PUHF}) \rangle = 0.75$ are given in Table III, and the corresponding spin populations

$$N(\mathrm{CPUHF}) = N(\mathrm{UHF})/K(0.75) \qquad (3)$$

are given in Tables V–VII.

In contrast to σ radicals[2,7–10], in our systems the quotients $Q = a_\mathrm{H}/N$ calculated at various levels differ substantially for the various systems and for the various positions within each system (Tables V–VII). With regard to this, our systems have to be divided into several groups with respect to

a) the hydroxyl group position (α-, β- and mixed α,β-hydroxyanthrasemiquinones)

b) the relevant C atom position in the aromatic skeleton (α- or β-position)

c) the relevant C atom position with respect to the hydroxyl group (neighboring OH, non-neighboring OH at the same ring and without any OH at the same ring)

d) the sign of the dominant spin density at the relevant C atom (positive or negative).

Now it is noteworthy that there exist two types of spin distribution in the systems under study: in the A1, A18, A1458, B2, B27, C1257 and C1368 systems the positive

TABLE IV
Statistical parameters R^2 and standard errors σ of K_calc for various parametrizations *k* of Eq. (*2*)

k	A_1	A_2	A_{12}	*B*	R^2	σ
1	6.4 ± 0.3	–	–	–2.88 ± 0.12	0.97694	0.121
2	–	5.80 ± 0.09	–	–1.06 ± 0.04	0.99727	0.042
3	–	–	2.80 ± 0.04	1.35 ± 0.04	0.99720	0.042
4	–1.5 ± 0.7	7.1 ± 0.7	–	–0.61 ± 0.04	0.99802	0.037
5	–4.55 ± 0.13	–15.5 ± 0.8	12.3 ± 0.4	10.866 ± 0.004	0.99998	0.004

TABLE V
Quotients $Q = a_H/N$ (in 10^{-4} T) calculated at various levels and extrapolated CPUHF spin populations N(CPUHF) for C atoms in various positions n of α-hydroxyanthrasemiquinones

System	n	Q(ROHF)	Q(UHF)	Q(PUHF)	N(CPUHF)	Q(CPUHF)
α Position with an OH on the ring, positive spin density						
A15	4	55.54	82.53	309.2	0.00286	328.8
α Position with an OH on the ring, negative spin density						
A1	4	71.92	–48.69	–200.4	–0.00487	–213.6
A15	8	55.10	–51.54	–193.0	–0.00458	–205.3
A18	4	65.90	–39.91	–204.0	–0.00451	–204.0
A18	5	63.10	–39.38	–201.3	–0.00457	–201.3
A145	8	52.53	–38.34	–199.1	–0.00430	–197.6
Average		62 ± 7	–44 ± 5	–200 ± 4		–204 ± 5
α Position with no OH on the ring, positive spin density						
A1	8	50.58	48.04	198.2	0.00308	210.8
A14	5	46.65	46.65	189.3	0.00263	201.6
Average		49 ± 2	47.4 ± 0.7	194 ± 4		206 ± 5
α Position with no OH on the ring, negative spin density						
A1	5	50.86	–28.00	–115.2	–0.00407	–122.8
A14	8	47.11	–34.35	–139.1	–0.00357	–148.4
Average		49 ± 2	–31 ± 3	–127 ± 12		–136 ± 13
β Position with a neighboring OH on the ring, positive spin density						
A14	2	34.73	93.38	378.3	0.00528	403.6
A15	2	33.54	102.27	383.4	0.00420	407.5
A145	2	32.42	79.08	410.4	0.00483	407.5
A1458	3	33.74	77.41	401.3	0.00464	398.8
A1458	6	32.58	78.46	407.5	0.00458	404.3
Average		33 ± 1	86 ± 10	396 ± 13		404 ± 3
β Position with a neighbouring OH on the ring, negative spin density						
A1	2	30.86	–95.50	–393.5	–0.00375	–419.0
A14	3	34.91	–128.93	–522.1	–0.00382	–557.2
A15	6	32.77	–135.28	–507.4	–0.00317	–539.0
A18	2	35.75	–87.41	–446.8	–0.00376	–446.8
A18	7	34.58	–89.79	–459.0	–0.00366	–459.0
A145	3	36.01	–104.30	–542.1	–0.00383	–537.5
A145	6	34.85	–92.34	–479.5	–0.00345	–475.9
A1458	2	33.80	–99.09	–513.9	–0.00362	–510.6
A1458	7	32.46	–102.78	–533.1	–0.00349	–529.6
Average		34 ± 2	–104 ± 16	–490 ± 50		–500 ± 50

TABLE V
(*Continued*)

System	*n*	*Q*(ROHF)	*Q*(UHF)	*Q*(PUHF)	*N*(CPUHF)	*Q*(CPUHF)
		β Position with a non-neighboring OH on the ring, positive spin density				
A1	3	21.37	55.82	229.9	0.00478	244.9
A15	7	26.39	76.14	285.4	0.00445	303.4
A18	3	23.61	55.95	286.0	0.00444	286.0
A18	6	22.92	56.07	286.7	0.00443	286.6
A145	7	26.20	60.35	313.3	0.00418	311.0
Average		24 ± 2	61 ± 8	280 ± 30		290 ± 20
		β Position with a non-neighboring OH on the ring, negative spin density				
A15	3	27.22	–128.69	–482.1	–0.00263	–512.7
		β Position with no OH on the ring, positive spin density				
A1	6	17.09	47.67	196.3	0.00411	209.2
A14	7	20.72	58.33	236.4	0.00361	252.1
Average		19 ± 2	53 ± 5	216 ± 19		230 ± 20
		β Position with no OH on the ring, negative spin density				
A1	7	23.91	–82.45	–339.6	–0.00301	–361.8
A14	6	20.81	–83.03	–337.0	–0.00254	–358.8
Average		22 ± 2	–82.7 ± 0.3	–338.4 ± 1.3		–360.3 ± 1.5

spin density dominates at the 1, 3, 6 and 8 positions while the negative spin density dominates at the 2, 4, 5 and 7 positions, whereas the reverse is true of the A14, A15, A145, B23, B26, B2367 and C1256 systems (see Table II).

Table V gives the quotients $Q = a_H/N$ for various levels of calculated spin populations at the relevant C atoms in α-hydroxyanthrasemiquinones. Except for the ROHF level, the quotients depend significantly on the spin density sign. The *Q* values for C atoms in the β positions with a dominant positive spin density are about 20–40% lower than in the case of a dominant negative spin density, whereas the reverse is true for C atoms in the α positions. Generally, the CPUHF data exhibit the lowest deviations from the average value. This fact seems to indicate correctness of the proposed method of CPUHF spin density evaluation. The decrease in the *Q* values with increasing distance between the C atom and the hydroxyl group may be connected with solvent effects supported by the hydroxyl group in real systems.

TABLE VI
Quotients $Q = a_H/N$ (in 10^{-4} T) calculated at various levels and extrapolated CPUHF spin populations N(CPUHF) for C atoms in various positions n of β-hydroxyanthrasemiquinones

System	n	Q(ROHF)	Q(UHF)	Q(PUHF)	N(CPUHF)	Q(CPUHF)
α Position with a neighboring OH on the ring, positive spin density						
B2	1	90.86	111.26	413.9	0.003669	438.9
B23	4	102.37	71.13	286.3	0.004386	305.5
B26	5	54.63	72.84	277.1	0.003118	295.0
B27	1	38.82	44.55	179.7	0.003965	191.6
B27	8	36.61	45.54	183.6	0.003879	195.9
B2367	4	146.25	95.91	477.0	0.004083	482.5
B2367	5	141.42	98.60	490.0	0.003971	496.0
α Position with a neighboring OH on the ring, negative spin density						
B23	1	106.52	–63.57	–255.7	–0.004908	–273.0
B26	1	57.50	–49.07	–186.6	–0.004629	–198.7
B2367	1	150.38	–87.87	–436.8	–0.004457	–442.0
B2367	8	143.06	–88.94	–441.7	–0.004403	–447.4
α Position with a non-neighboring OH on the ring, positive spin density						
B26	4	191.85	114.45	436.0	0.003451	463.5
α Position with a non-neighboring OH on the ring, negative spin density						
B2	4	39.36	–16.35	–60.8	0.004186	–64.5
B26	8	187.13	–103.49	–394.1	–0.003817	–419.2
B27	4	301.56	–94.87	–382.4	–0.004263	–408.2
B27	5	289.04	–94.57	–381.6	–0.004277	–406.8
α Position with no OH on the ring, positive spin density						
B2	8	156.42	170.14	632.3	0.002921	670.9
B23	5	101.97	106.74	430.2	0.002486	458.4
α Position with no OH on the ring, negative spin density						
B2	5	15.86	–9.08	–33.8	–0.004189	–35.8
B23	8	103.83	–71.74	–288.6	–0.003699	–308.1
β Position with a neighboring OH on the ring, positive spin density						
B2	3	11.77	32.35	120.3	0.004232	127.6
B26	7	0.00	0.00	0.0	0.003787	0.0
B27	3	54.70	138.67	559.1	0.004358	596.5
B27	6	52.19	139.41	561.6	0.004335	599.7
β Position with a neighboring OH on the ring, negative spin density						
B26	3	0.00	0.00	0.0	–0.003624	0.0

TABLE VI
(*Continued*)

System	*n*	*Q*(ROHF)	*Q*(UHF)	*Q*(PUHF)	*N*(CPUHF)	*Q*(CPUHF)
		β Position with no OH on the ring, positive spin density				
B2	6	19.57	61.60	228.9	0.004240	242.9
B23	7	12.19	38.05	153.3	0.003732	163.4
		β Position with no OH on the ring, negative spin density				
B2	7	13.00	–54.20	–201.3	–0.002901	–213.7
B23	6	12.28	–57.66	–231.9	–0.002463	–247.6

TABLE VII
Quotients $Q = a_H/N$ (in 10^{-4} T) calculated at various levels and extrapolated CPUHF spin populations *N*(CPUHF) for C atoms in various positions *n* of α,β-hydroxyanthrasemiquinones

System	*n*	*Q*(ROHF)	*Q*(UHF)	*Q*(PUHF)	*N*(CPUHF)	*Q*(CPUHF)
		α Position with a neighboring OH on the ring, negative spin density				
C1368	4	51.00	–49.31	–269.3	–0.004409	–260.8
C1368	5	49.81	–47.84	–261.4	–0.004546	–253.0
		β Position with a neighboring OH on the ring, positive spin density				
C1256	7	6.61	14.39	72.1	0.004124	72.7
C1258	3	37.66	73.47	447.9	0.004216	407.9
C1258	6	40.95	96.24	587.1	0.004603	534.4
		β Position with a neighboring OH on the ring, negative spin density				
C1256	3	6.84	–15.81	–79.4	–0.003752	–79.9
C1258	7	7.09	–18.68	–114.1	–0.003663	–103.7
C1368	2	80.82	–162.80	–889.5	–0.003833	–860.9
C1368	7	73.43	–170.45	–932.2	–0.003661	–901.4
		β Position with a non-neighboring OH on the ring, positive spin density				
C1256	4	142.96	104.20	522.7	0.003720	526.8
		β Position with a non-neighboring OH on the ring, negative spin density				
C1256	8	138.32	–88.77	–445.5	–0.004367	–448.8
C1258	4	138.69	–70.23	–428.6	–0.004385	–389.9

The situation for β-hydroxyanthrasemiquinones (Table VI) seems to be chaotic. Our data suggest higher a_H values for positions 3, 4 and 5 in B2, 1 (4) in B23, 1 (5) and 3 (7) in B26, and 1 (8) in B27, whereas for positions 8 in B2 and 3 (6) in B27 the a_H values should be lower. As our calculations are in a good agreement with the experimental data for α-hydroxyanthrasemiquinones, and the a_H values derived from complicated EPR spectra do not always lead to unambiguous conclusions (dubious results are even obtained from extensive simulations), re-examination of the experimental data is is desirable. Moreover, the a_H values for the B27 system were not measured but only assigned by applying the additivity principles, and assignment verification based on the additivity principles for β-hydroxyanthrasemiquinones is not so accurate as for α-hydroxyanthrasemiquinones[1]. A similar situation occurs in the case of α,β-hydroxyanthrasemiquinones (Table VII). Our data indicate a reverse assignment in C1368 as well as higher a_H values for positions 3 (7) in C1256 and 7 in C1258.

In contrast to neutral hydroxyquinones without spin polarization, hydroxyanthrasemiquinones are systems where the symmetry of atomic configuration does not correspond with the symmetry of electronic structure (alternating spin density – see, for example, Table II). As a consequence, the nuclear skeleton lowers its symmetry. On the other hand, quantum-chemical calculations may lead to minor distortions of the system

TABLE VIII
Relative deviations δ (in %) from the averaged values of calculated spin populations at various levels for equivalent C atom positions n_1 and n_2 in the systems under study

System	n_1	n_2	ROHF	UHF, CPUHF	PUHF
		Positive spin density			
A18	3	6	1.48	0.11	0.11
A1458	3	6	1.75	0.67	0.77
B27	1	8	2.93	1.10	1.08
B27	3	6	2.35	0.27	0.22
B2367	4	5	1.68	1.38	1.35
		Negative spin density			
A18	2	7	1.66	1.34	1.35
A18	4	5	2.17	0.67	0.66
A1458	2	7	2.02	1.83	1.84
B27	4	5	2.12	0.16	0.11
B2367	1	8	2.49	0.61	0.56
C1368	2	7	4.79	2.30	2.34
C1368	4	5	1.18	1.52	1.50

symmetry for numerical reasons (e.g. a higher precision in the SCF procedure or smaller gradient thresholds during geometry optimization are desirable). The quality of our calculations is illustrated by Table VIII. It is evident that our calculation error is less than 5% and largely less than 2%. Hence, this error cannot account for the differences between the experimental and AM1 calculated data.

CONCLUSIONS

Our results indicate that the relation between the spin distribution data obtained by analysis of the EPR spectra and by quantum-chemical calculations depends on the position of the C atom within the aromatic skeleton, on its spin density sign and on its position relative to hydroxyl substituents. Complete annihilation of higher spin state contaminations based on a polynomial extrapolation with respect to the $\langle \hat{S}^2 \rangle$ values brings about a higher quality of spin evaluation but fails to eliminate the significant discrepancies between the theoretical and experimental data; these may be partly explained by asymmetry of solvent effects caused by hydroxyl groups and to a lesser extent by calculation errors. A wrong evaluation of experimental EPR spectra may be responsible as well.

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