Theoret. Chim. Acta (Berl.) 53, 309–317 (1979)

THEORETICA CHIMICA ACTA

Additivity Model Calculations of UHF Spin Densities and Charge Densities in Methyl-Substituted Radical Cations

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By use of a heteroatom model for the methyl group and an additivity model for spin densities, the unrestricted Hartree–Fock after annihilation (UHFAA) results for the radical cations of naphthalene, 1-methylnaphthalene and 2-methylnaphthalene are used to predict the spin densities in the π-electron approximation in the corresponding cations of di-, tri- and tetramethylnaphthalenes. The additivity model approach is shown to be equally successful for charge densities.

Key words: Additivity model – UHF spin densities and charge densities – Heteroatom model – Radical cations

1. Introduction

The methyl-substituted radical anions and radical cations form a relatively simple series of radicals in which the perturbing effect of substituents on spin and charge densities can be correlated with theoretical calculations on the electronic structures of radical species [1–4]. Such correlations facilitate the interpretation of experimental results and provide a model in terms of which the systematic behaviour, if any, of various substituents may be understood. In many instances, however, the agreement between theory and experiment is poor. In semi-empirical calculations this may be due to deficiencies in the method or to the arbitrary choice of the numerical values for the inevitable parameters. In π-electron calculations on methyl-substituted species an appropriate model must be adopted for the methyl group. Careful consideration of the latter point is essential if the effect of the methyl group on observables is to be accounted for by a method which treats only the π-electrons explicitly.

0040-5744/79/0053/0309/$01.80

Moss *et al.* [5, 6] have used inductive and inductive-hyperconjugative models to study the effect of the methyl group in the radical anions of methylnaphthalenes. By use of the McLachlan method they have shown the additivity of spin density values. More recently [7] the additivity model suggested by the results of Moss *et al.* has been employed to predict UHF spin densities in some methyl-substituted radical anions. In the present study the UHF spin densities and charge densities in the radical cations of methyl-substituted naphthalenes are predicted with considerable accuracy by use of the additivity model. This simple model is attractive in the sense that the UHF results for the radical cations of naphthalene, 1-methylnaphthalene and 2-methylnaphthalene are sufficient for the prediction, by use of the additivity model, of the UHF spin densities and charge densities in the radical cations of dimethyl, trimethyl and tetramethylnaphthalenes. The methyl group is treated in the present work by use of a heteroatom model.

2. Method of Calculation

As in our previous work based on the π-electron approximation, the spin densities and charge densities were calculated by use of the unrestricted Hartree–Fock (UHF) method of Amos and Snyder [8] with the appropriate parameters for the pseudo heteroatom and valence state data from Hinze and Jaffé [9]. The Ohno [10] and Linderberg [11] formulas were employed. Effective nuclear charges were taken from the work of Mulliken *et al.* [12] and parameters for the starting density matrices from Streitwieser [13].

3. Results and Discussion

The changes in proton splittings due to methyl-substitution obey an additivity relation [6]. In particular, substitution of a methyl group at position 1 (see Fig. 1) of the naphthalene cation produces changes in the splittings at the 2, 3, 4, 5, 6, 7, and 8 positions [14]. These changes are conveniently designated by *b*, *c*, *d*, *e*, *f*, *g*, and *h*, respectively. Similarly the substitution of a methyl group at position 2 causes changes in the splittings at the 1, 3, 4, 5, 6, 7, and 8 positions. These changes are designated by a', c', d', e', f', g' and h', respectively. Application of the additivity model to the prediction of the spin density for methyl substitution at the various positions leads directly to the expressions given in Table 1. From the computed spin densities of the 1-methyl- and 2-methylnaphthalene radical cations, the constants *b*, *c*, etc. and a', c', etc. can be evaluated. The values of these constants are reported in Table 2.

In Table 3 the additivity model expressions for ρ_i, the additivity model value of ρ_i (under column I) and the UHFAA value of ρ_i (under column II) are listed for

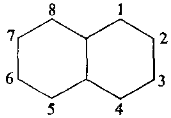

Fig. 1. Numbering scheme for naphthalene derivatives

Table 1. Calculated spin densities in 1-methylnaphthalene and 2-methylnaphthalene radical cations

System	Position	Expression for ρ_i	ρ_i
1-methylnaphthalene	2	$b + \beta$	0.0935
	3	$c + \beta$	0.0337
	4	$d + \alpha$	0.2680
	5	$e + \alpha$	0.1753
	6	$f + \beta$	0.0226
	7	$g + \beta$	0.0557
	8	$h + \alpha$	0.1415
2-methylnaphthalene	1	$a' + \alpha$	0.2708
	3	$c' + \beta$	—0.0030
	4	$d' + \alpha$	0.1782
	5	$e' + \alpha$	0.1521
	6	$f' + \beta$	0.0917
	7	$g' + \beta$	0.0067
	8	$h' + \alpha$	0.2269

many methylnaphthalenes. The spin densities obtained by application of the simple additivity model agree well with the values obtained from the complete UHFAA calculations. In this context it is interesting to note that the magnitude of the parameters in Table 2 ranges from about 0.01 to 0.07 while the discrepancy between UHFAA and additivity model values of ρ_i is usually less than 0.01.

The additivity model can also be applied to the UHF charge densities in these systems. The additivity model expressions and UHF values for the charge densities in the 1-methyl- and 2-methylnaphthalene radical cations are given in Table 4. The values of the parameters b_1, c_1, d_1, e_1, f_1, g_1, h_1, a'_1, c'_1, d'_1, e'_1, f'_1, g'_1, and h'_1 are listed in Table 5. Although the charge density parameters extend over a similar range of magnitude as the spin density parameters there is no obvious relationship

Table 2. Calculated spin density parameters[a]

b	0.0438
c	—0.0160
d	0.0547
e	—0.0380
f	—0.0277
g	0.0060
h	—0.0718
a'	0.0575
c'	—0.0527
d'	—0.0351
e'	—0.0612
f'	0.0420
g'	—0.0430
h'	0.0136

[a] Obtained by use of the calculated spin densities for the naphthalene radical cation ($\alpha = 0.2133$ and $\beta = 0.0497$).

Table 3. Spin densities in methyl-substituted naphthalene radical cations[a]

System	Position	Expression for ρ_i	ρ_i	
			I	II
1,2-dimethylnaphthalene	3	$c + c' + \beta$	—0.0190	—0.0114
	4	$d + d' + \alpha$	0.2329	0.2205
	5	$e + e' + \alpha$	0.1633	0.1240
	6	$f + f' + \beta$	0.0640	0.0527
	7	$g + g' + \beta$	0.0127	0.0189
	8	$h + h' + \alpha$	0.1551	0.1544
1,3-dimethylnaphthalene	2	$b + c' + \beta$	0.0408	0.0331
	4	$a' + d + \alpha$	0.3255	0.3266
	5	$e + h' + \alpha$	0.1889	0.1959
	6	$f + g' + \beta$	0.0210	—0.0052
	7	$f' + g + \beta$	0.0977	0.0891
	8	$e' + h + \alpha$	0.0814	0.1037
1,4-dimethylnaphthalene	2	$b + c + \beta$	0.0775	0.0726
	5	$e + h + \alpha$	0.1035	0.1180
	6	$f + g + \beta$	0.0280	0.0302
1,5-dimethylnaphthalene	2	$b + f + \beta$	0.0658	0.0603
	3	$c + g + \beta$	0.0397	0.0446
	4	$d + h + \alpha$	0.1962	0.2011
1,6-dimethylnaphthalene	2	$b + f' + \beta$	0.1355	0.1166
	3	$c + g' + \beta$	0.0093	0.0147
	4	$d + h' + \alpha$	0.2816	0.2808
	5	$a' + e + \alpha$	0.2328	0.2077
	7	$c' + g + \beta$	0.0300	0.0281
	8	$d' + h + \alpha$	0.1064	0.1331
1,8-dimethylnaphthalene	2	$b + g + \beta$	0.0995	0.0937
	3	$c + f + \beta$	0.0060	0.0059
	4	$d + e + \alpha$	0.2300	0.2344
2,3-dimethylnaphthalene	1	$a' + a' + \alpha$	0.2357	0.2409
	5	$e' + h' + \alpha$	0.1657	0.1938
	6	$f' + g' + \beta$	0.0487	0.0477
2,6-dimethylnaphthalene	1	$a' + e' + \alpha$	0.2096	0.2207
	3	$c' + g' + \beta$	0.0460	—0.0201
	4	$d' + h' + \alpha$	0.1918	0.1835
2,7-dimethylnaphthalene	1	$a' + h' + \alpha$	0.2844	0.2855
	3	$c' + f' + \beta$	0.0390	0.0216
	4	$d' + e' + \alpha$	0.1170	0.1503
1,2,4,-trimethylnaphthalene	3	$b + c + c' + \beta$	0.0248	0.0227
	5	$e + e' + h + \alpha$	0.0423	0.0854
	6	$f + f' + g + \beta$	0.0700	0.0554
	7	$f + g + g' + \beta$	0.0150	0.0058
	8	$e + h + h' + \alpha$	0.1165	0.1363

Table 3 (Continued)

System	Position	Expression for ρ_i	ρ_i	
			I	II
1,4,5-trimethylnaphthalene	2	$b + c + f + \beta$	0.0498	0.0515
	3	$b + c + g + \beta$	0.0835	0.0799
	6	$b + f + g + \beta$	0.0718	0.0613
	7	$c + f + g + \beta$	0.0120	0.0247
	8	$d + e + h + \alpha$	0.1582	0.1700
1,2,6-trimethylnaphthalene	3	$c + c' + g' + \beta$	0.0620	0.0235
	4	$d + d' + h' + \alpha$	0.2459	0.2296
	5	$e + e' + a' + \alpha$	0.1716	0.1507
	7	$c' + g + g' + \beta$	—0.0400	0.0010
	8	$d' + h + h' + \alpha$	0.1200	0.1429
1,6,7-trimethylnaphthalene	2	$b + f' + g' + \beta$	0.0925	0.0875
	3	$c + f' + g' + \beta$	0.0327	0.0365
	4	$d + e' + h' + \alpha$	0.2204	0.2538
	5	$a' + d' + e + \alpha$	0.1977	0.1935
	8	$a' + d' + h + \alpha$	0.1639	0.1620
2,3,6-trimethylnaphthalene	1	$a' + d' + e' + \alpha$	0.1736	0.2041
	4	$a' + d' + h' + \alpha$	0.2493	0.2424
	5	$a' + e' + h' + \alpha$	0.2232	0.2186
	7	$c + f' + g' + \beta$	0.0327	0.0046
	8	$d' + e' + h' + \alpha$	0.1306	0.1822
1,2,3,4-tetramethylnaphthalene	5	$e + e' + h + h' + \alpha$	0.0559	0.1112
	6	$f + f' + g + g' + \beta$	0.0270	0.0305
1,2,5,6-tetramethylnaphthalene	3	$c + c' + g + g' + \beta$	—0.0560	0.0074
	4	$d + d' + h + h' + \alpha$	0.1747	0.1846

[a] Values under I were calculated from an additivity model and the values under II were obtained from UHFAA calculations.

Table 4. Calculated charge densities in 1-methylnaphthalene and 2-methylnaphthalene radical cations

System	Position	Expression for q_i(res)	q_i(res)
1-methylnaphthalene	2	$b_1 + \delta$	0.0499
	3	$c_1 + \delta$	0.0933
	4	$d_1 + \gamma$	0.1837
	5	$e_1 + \gamma$	0.1446
	6	$f_1 + \delta$	0.0845
	7	$g_1 + \delta$	0.0873
	8	$h_1 + \gamma$	0.1371
2-methylnaphthalene	1	$a'_1 + \gamma$	0.1390
	3	$c'_1 + \delta$	—0.0113
	4	$d'_1 + \gamma$	0.2072
	5	$e'_1 + \delta$	0.1672
	6	$f'_1 + \delta$	0.1012
	7	$g'_1 + \delta$	0.0688
	8	$h'_1 + \gamma$	0.1657

Table 5. Calculated charge density parameters[a]

b_1	—0.0386
c_1	0.0018
d_1	—0.0038
e_1	—0.0429
f_1	—0.0040
g_1	—0.0012
h_1	—0.0504
a_1'	—0.0485
c_1'	—0.0772
d_1'	0.0197
e_1'	—0.0203
f_1'	0.0127
g_1'	—0.0197
h_1'	—0.0218

[a] Obtained by use of the calculated charge densities for the naphthalene radical cation ($\gamma = 0.1875$ and $\delta = 0.0885$).

between the two sets of additivity parameters. Thus a relatively high additivity parameter for spin density (e.g. $d = 0.0547$) does not preclude a low charge density parameter at the same position (e.g. $d_1 = -0.0038$) nor a large change in direction of the parameter (e.g. $b = 0.0438$ versus $b_1 = -0.0386$). However the spin and charge densities display similar trends. The spin density at the 1 position of the

Table 6. Charge densities in methyl-substituted naphthalene cations[a]

System	Position	Expression for q_i(res)	q_i(res) I	q_i(res) II
1,2-dimethylnaphthalene	3	$c_1 + c_1' + \delta$	—0.0095	—0.0054
	4	$d_1 + d_1' + \gamma$	0.2034	0.2013
	5	$e_1 + e_1' + \gamma$	0.1243	0.1291
	6	$f_1 + f_1' + \delta$	0.0972	0.0908
	7	$g_1 + g_1' + \delta$	0.0676	0.0775
	8	$h_1 + h_1' + \gamma$	0.1153	0.1193
1,3-dimethylnaphthalene	2	$b_1 + c_1' + \delta$	—0.0493	—0.0491
	4	$d_1 + a_1' + \gamma$	0.1352	0.1346
	5	$e_1 + h_1' + \gamma$	0.1228	0.1260
	6	$f_1 + g_1' + \delta$	0.0648	0.0730
	7	$f_1' + g_1 + \delta$	0.1000	0.0922
	8	$e_1' + h_1 + \gamma$	0.1168	0.1287
1,4-dimethylnaphthalene	2	$b_1 + c_1 + \delta$	0.0517	0.0529
	5	$e_1 + h_1 + \gamma$	0.0942	0.1046
	6	$f_1 + g_1 + \delta$	0.0833	0.0828
1,5-dimethylnaphthalene	2	$b_1 + f_1 + \delta$	0.0459	0.0462
	3	$c_1 + g_1 + \delta$	0.0891	0.0982
	4	$d_1 + h_1 + \gamma$	0.1333	0.1417
1,6-dimethylnaphthalene	2	$b_1 + f_1' + \delta$	0.0626	0.0527
	3	$c_1 + g_1' + \delta$	0.0706	0.0821
	4	$d_1 + h_1' + \gamma$	0.1619	0.1725
	5	$a_1' + e_1 + \gamma$	0.0961	0.1122
	7	$c' + g + \delta$	0.0125	0.0294
	8	$d_1' + h_1 + \gamma$	0.1568	0.1573

Table 6 (Continued)

System	Position	Expression for q_i(res)	q_i(res) I	q_i(res) II
1,8-dimethylnaphthalene	2	$b_1 + g_1 + \delta$	0.0487	0.0446
	3	$c_1 + f_1 + \delta$	0.0863	0.0925
	4	$d_1 + e_1 + \gamma$	0.1408	0.1460
2,3-dimethylnaphthalene	1	$a_1' + d_1' + \gamma$	0.1587	0.1610
	5	$e_1' + h_1' + \gamma$	0.1454	0.1682
	6	$f_1' + g_1' + \delta$	0.0815	0.0811
2,6-dimethylnaphthalene	1	$a_1' + e_1' + \gamma$	0.1187	0.1240
	3	$c_1' + g_1' + \delta$	0.0084	0.0149
	4	$d_1' + h_1' + \gamma$	0.1854	0.1886
2,7-dimethylnaphthalene	1	$a_1' + h_1' + \gamma$	0.1172	0.1224
	3	$c_1' + f_1' + \delta$	0.0014	0.0016
	4	$d_1' + e_1' + \gamma$	0.1869	0.2050
1,2,4-trimethylnaphthalene	3	$b_1 + c_1 + c_1' + \delta$	0.0475	0.0418
	5	$e_1 + e_1' + h_1 + \gamma$	0.0739	0.0996
	6	$f_1 + f_1' + g_1 + \delta$	0.0960	0.0807
	7	$f_1 + g_1 + g_1' + \delta$	0.0636	0.0756
	8	$e_1 + h_1 + h_1' + \gamma$	0.0724	0.0991
1,4,5-trimethylnaphthalene	2	$b_1 + c_1 + f_1 + \delta$	−0.0478	0.0536
	3	$b_1 + c_1 + g_1 + \delta$	0.0505	0.0507
	6	$b_1 + f_1 + g_1 + \delta$	0.0447	0.0388
	7	$c_1 + f_1 + g_1 + \delta$	0.0851	0.0981
	8	$d_1 + e_1 + h_1 + \gamma$	0.0904	0.1049
1,2,6-trimethylnaphthalene	3	$c_1 + c_1' + g_1' + \delta$	−0.0066	−0.0059
	4	$d_1 + d_1' + h_1' + \gamma$	0.1816	0.1865
	5	$e_1 + e_1' + a_1' + \gamma$	0.0758	0.0946
	7	$c_1' + g_1 + g_1' + \delta$	0.0096	0.0212
	8	$d_1' + h_1 + h_1' + \gamma$	0.1460	0.1372
1,6,7-trimethylnaphthalene	2	$b_1 + f_1' + g_1' + \delta$	0.0429	0.0427
	3	$c_1 + f_1' + g_1' + \delta$	0.0833	0.0884
	4	$d_1 + e_1' + h_1' + \gamma$	0.1416	0.1714
	5	$a_1' + d_1' + e_1 + \gamma$	0.1158	0.1275
	8	$a_1' + d_1' + h_1 + \gamma$	0.1083	0.1215
2,3,6-trimethylnaphthalene	1	$a_1' + d_1' + e_1' + \gamma$	0.1384	0.1498
	4	$a_1' + d_1' + h_1' + \gamma$	0.1369	0.1457
	5	$a_1' + e_1' + h_1' + \gamma$	0.0969	0.1318
	7	$c_1' + f_1' + f_1' + \delta$	0.0043	0.0095
	8	$d_1' + e_1' + h_1' + \gamma$	0.1651	0.1853
1,2,3,4-tetramethylnaphthalene	5	$e_1 + e_1' + h_1 + h_1' + \gamma$	0.0521	0.0959
	6	$f_1 + f_1' + g_1 + g_1' + \delta$	0.0843	0.0764
1,2,5,6-tetramethylnaphthalene	3	$c_1 + c_1' + g_1 + g_1' + \delta$	0.0078	0.0051
	4	$d_1 + d_1' + h_1 + h_1' + \gamma$	0.1312	0.1564

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[a] I and II refer to the additivity model and UHFAA results, respectively.

Table 7. UHFAA spin densities on the carbon attached to the methyl group

System	Expression for ρ_i^a	ρ_i
1-methylnaphthalene	A	0.2000
1,4-dimethylnaphthalene	$A + D$	0.2397
1,5-dimethylnaphthalene	$A + E$	0.1759
1,8-dimethylnaphthalene	$A + H$	0.1442
2-methylnaphthalene	B	0.0859
2,3-dimethylnaphthalene	$B + C$	0.0295
2,6-dimethylnaphthalene	$B + F$	0.1095
2,7-dimethylnaphthalene	$B + G$	0.0545

[a] $C = -0.0564$, $D = 0.0397$, $E = -0.0241$, $F = 0.0236$, $G = -0.0314$, $H = -0.0558$.

naphthalene radical cation is much greater than the 2 position: 0.2133 versus 0.0497. The same trend is observed for the charge density of the naphthalene radical cation: 0.1875 at the 1 position versus 0.0885 at the 2 position. Moreover there is a close correlation between the trends of the spin densities in the 1-methylnaphthalene and 2-methylnaphthalene radical cations and the corresponding charge densities (cf. Tables 1 and 4). From the data presented in Table 6 for many radical cations, it is clear that charge densities, like spin densities, can be predicted successfully by use of an additivity model. Again the magnitude of the additivity parameters is normally larger than the deviations between the two sets of charge densities.

And finally we turn our attention to the hyperfine splittings due to the protons of the methyl group. The methyl proton splitting $a_{\mathrm{Me}}^{\mathrm{H}}(n)$ for the methyl group attached to carbon atom n is proportional to the spin density ρ_n on atom n. The proportionality constant $Q_{\mathrm{CCH_3}}^{\mathrm{H}}$ is a positive constant. For the radical cations of methyl-substituted condensed benzenoids $Q_{\mathrm{CCH_3}}^{\mathrm{H}}$ is 44 gauss [15]. Once again an additivity model may be constructed successfully. Let the spin density at the 1 position of the 1-methylnaphthalene cation be designated by A. Also let the parameters D, E, and H represent the changes produced in the spin density by methyl substitution at the 4, 5, and 8 positions, respectively. Similar expressions are also given for the spin densities in the β substituted naphthalene cations where B is the spin density at position 2 of the 2-methylnaphthalene cation. Also C, F, and G are the appropriate parameters for methyl substitution at the 3, 6, and 7 positions, respectively. These parameters, evaluated from the data given in Table 7, predict that the spin density $(A + D + E + H)$ at the 1 position of the 1,4,5,8-tetramethylnaphthalene cation is 0.1698 and that the spin density $(B + C + F + G)$ at the 2 position of the 2,3,6,7-tetramethylnaphthalene cation is 0.0217. This is in agreement with the UHFAA values of 0.1711 and 0.0298, respectively.

In conclusion we note that, with a heteroatom model for the methyl group, the UHF ring position and methyl proton spin densities as well as the charge densities of a series of methyl-substituted radical cations can be predicted reliably by a simple additivity model. As such models have considerable intuitive appeal it would be interesting to establish the extent to which these observations may be generalized.

Acknowledgement. The financial support of the Natural Sciences and Engineering Research Council of Canada and the Research Development Fund of Dalhousie University is gratefully acknowledged.

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Received April 27, 1979/July 3, 1979