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SCF-π-Electron Calculations Using Orthogonalised Atomic Orbitals

IV. Non-Empirical Calculations for Open-Shell Systems

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The non-empirical SCF-LCAO-π-electron method previously developed for closed-shell molecules is extended to treat open-shell hydrocarbon systems. It is shown that the use of the Roothaan formalism, with configuration interaction involving all singly excited states, leads to a satisfactory description of the doublet state excitation energies and of the spin density distributions. Comparison of the total π-electronic energies with values relating to the corresponding closed-shell systems yields ionisation potentials in good agreement with experimental data.

Die früher entwickelte nichtempirische SCF-LCAO-Elektronenmethode, die für die Behandlung von Molekülen mit abgeschlossenen Schalen geeignet war, wird für die Anwendung auf Kohlenwasserstoffe mit offenen Schalen erweitert. Es wird gezeigt, daß der Roothaansche Formalismus mit Konfigurationswechselwirkung aller einfach angeregten Zustände zu einer befriedigenden Beschreibung der Anregungsenergien von Dublet-Zuständen sowie der Spindichteverteilung führt. Ein Vergleich der Gesamtenergie des π-Elektronensystems mit den entsprechenden Werten des zugehörigen Moleküls mit abgeschlossenen Schalen ergibt Ionisationspotentiale, die mit den experimentellen Daten gut übereinstimmen.

La méthode SCF LCAO π non empirique développée précédemment pour les molécules à couches fermées est étendue au traitement des systèmes d'hydrocarbures à couches ouvertes. L'emploi du formalisme de Roothan avec une interaction de configuration impliquant tous les états monoexcités conduit à une description satisfaisante des énergies d'excitation de l'état doublet et des densités de spin. La comparaison des énergies électroniques totales π avec les valeurs correspondantes dans les systèmes à couches fermées fournit des potentiels d'ionisation en bon accord avec les données expérimentales.

Introduction

In the previous paper of this series [1] we described a non-empirical SCF-π-electron method for closed-shell molecules in which an orthogonalised basis set of atomic orbitals was used. The procedure resembled the original Adams-Miller technique [2], but all the required parameters were found non-empirically, using $Z_C = 3.25$, and a proper distinction between localised and orthogonalised quantities was observed. The singlet state excitation energies obtained agreed extremely well with the experimental values, and we have therefore extended our method to treat the less well studied open-shell systems. We now report our calculations of doublet state excitation energies and spin density distributions for a number of radical and anion and cation systems, together with the ionisation potentials derived by comparison of the total π-electronic energies with those of the appropriate closed-shell molecules.

Method

The numerous unrestricted Hartree-Fock functions used to describe the ground states of open-shell systems are well known to be eigenfunctions only of the spin component, $\hat{S}_z$, and not of the total spin operator, $\hat{S}^2$. Such methods therefore relate to mixtures of states of different spin multiplicities, and are unsuitable for the calculation of doublet state excitation energies. Of the restricted methods that of Longuett-Higgins and Pople [3] contains approximations which do not precisely fulfil the conditions shown by Lefebvre [4] to be necessary for self-consistency, and we have therefore adopted the more complex but exact method due to Roothaan [5].

Within this framework our method of evaluation of the contributions to the Fock matrix, $\boldsymbol{F}$, is essentially similar to that used before [1]. One-centre repulsion integrals are derived using the Saturno [6] operator, two-centre integrals via the Mataga-Nishimoto [7] approximation, and three- and four-centre terms by use of the Mulliken approximation. Localised repulsion integrals are used for the $\boldsymbol{H}^0 \rightarrow \boldsymbol{H}$ conversion and orthogonalised quantities for that from $\boldsymbol{H}^\lambda$ to $\boldsymbol{F}$, whilst the $\boldsymbol{H}$ to $\boldsymbol{H}^\lambda$ transformation is achieved as before [1].

However, in many open-shell systems the charge densities at each carbon atom may differ appreciably from unity and we therefore incorporated a Variable Electronegativity (VE) routine (cf. Warren and Yandle [8]), in which quantities depending on the effective nuclear charge, Z, are recalculated at each cycle of the iteration. We assumed the Slater's rule variation with charge density, $Z_p = 3.60 - 0.35\ P_{pp}$, together with a quadratic dependence of the ionisation potential, $I_p = 0.3545\ Z_p^2 + 9.158\ Z_p - 22.349$, following Brown and Heffernan [9]. The one-centre integrals were then found using $(pp/pp) = (Z_p/9) \times 27.206$ eV, and the overlap and penetration integrals from the standard formulae [10, 11]. The two-centre repulsion integral, (pp/qq), $p \neq q$, using the Saturno operator is readily evaluated in terms of the general exponential integral via the method of Coulson [12] and as for the homonuclear case this is found to lead to values which closely parallel those predicted by the Mataga-Nishimoto expression.

Expressions for the total π-electronic energy of open-shell systems and for the elements of the Fock matrix have been given by Roothaan [5] and by Adams and Lykos [13], the latter formulae being valid subject to the Zero Differential Overlap approximation, a condition satisfied using an orthogonalised basis set. The Fock matrix thus derived was iterated to self-consistency in the usual way using programs written by us in FORTRAN IV, but to avoid non-convergence problems the VE routine was introduced only after a fairly close approach to self-consistency had been attained. Because of the complicated matrix expressions in the open-shell formulation it was also necessary to use double precision arithmetic to avert the accummulation of round-off errors.

For systems containing one open-shell for the formal ground state, G, there are four types of singly excited states which may arise. These are customarily denoted as A, B, C_α, and C_β respectively [14, 15] and the complete configuration interaction matrix elements connecting them and the ground state have been given by Zahradnik and Carsky [15]. An important distinction from the closed-shell case lies in the first order interaction between the ground and C_β type states, and thus, although optical transitions to C_β levels are formally forbidden, the $G - C_\beta$ interaction often results in significant (ca. 0.2 eV) depressions of the ground state energy. We have therefore included the ground and all singly excited states in our CI treatment, but we neglected doubly excited configurations since their inclusion has been shown to have little effect on either the doublet state excitation energies [16] or the spin density distribution [17]. Quartet state energies were not calculated since our previous experience [1, 18, 19] has shown that the Saturno operator and the Mataga-Nishimoto approximation are inappropriate for calculating the energies of the states of higher spin multiplicity.

The deficiencies of Koopmans' theorem for the calculation of ionisation potentials are well known and we therefore obtained these values by comparison of the total π-electronic energy of the ground state with that of the corresponding open-shell positive ion, the former value being derived according to Roothaan [20]. The IP's of the open-shell radicals were similarly found by comparison of the energies with those of the appropriate closed-shell positive ions. The complexity of our computer program precluded the inclusion of any Variable Bond Order (VBO) procedure, and the consequent assumption of the same geometry for both the closed and open-shell systems thus yields vertical rather than adiabatic values for the IP's. We have therefore compared our results with electron impact data where available, although experimentally these usually differ only slightly from the adiabatic values. Electron affinities were also calculated in a similar fashion.

Finally, we have calculated spin density distributions from our results, and, although UHF methods have been much more popular for this purpose, a recent study by Tino [21] has shown the Roothaan method to be only marginally poorer overall, and probably superior for positions with negative spin densities. In past applications of the restricted methods it has been assumed [21, 22] that only $G - C_\beta$ interactions need be included in this calculation, but for the Longuett-Higgins and Pople method this conclusion is dubious since Ishitani and Nagakura have shown [14] that the $G - A$ and $G - B$ elements of the CI matrix are non-vanishing. Furthermore, in our own calculations with the Roothaan method the eigenvectors of the doublet CI matrix show small but appreciable A and B type contributions to the ground state, even though all the $G - A$ and $G - B$ matrix elements are here necessarily zero. This is because although these elements vanish those connecting the C_β states with the other types do not [15], and the A, B and C_α configurations may contribute to the lowest level via a second order effect. Accordingly we included all contributions to the true ground state in our spin density calculations.

In our results the spin densities are expressed in terms of an orthogonalised basis set, but test calculations showed that conversion to a localised basis led only to very small changes. The charge densities behave similarly in this respect, but, unlike the spin densities are little affected by configuration interaction as shown by the results in Table 4.

Results and Discussion

In this Section we report our results for twelve systems – allyl$^\cdot$, pentadienyl$^\cdot$, heptatrienyl$^\cdot$, benzyl$^\cdot$, ethylene$\overset{-}{\cdot}$, butadiene$\overset{-}{\cdot}$, hexatriene$\overset{-}{\cdot}$, octatetraene$\overset{-}{\cdot}$, decapentaene$\overset{-}{\cdot}$, styrene$\overset{-}{\cdot}$, naphthalene$^{\pm\cdot}$, and azulene$^{\pm\cdot}$. For these systems doublet state excitation energies are recorded together with ionisation potentials for all the parent structures and electron affinities for systems in which the neutral molecule has a closed-shell structure. Also listed are the calculated spin density distributions for those systems for which experimental data are available – allyl$^\cdot$, benzyl$^\cdot$, butadiene$\overset{-}{\cdot}$, azulene$\overset{-}{\cdot}$, azulene$\overset{+}{\cdot}$, naphthalene$\overset{-}{\cdot}$, and naphthalene$\overset{+}{\cdot}$. The geometries used for the free radicals assume regular lengths of 1.40 Å throughout, with the 120° angle and the trans-conformation for the polyenes, whilst for the remaining molecules the same geometries were used as for the neutral systems treated earlier [1].

Doublet State Excitation Energies

In Table 1 are listed the calculated doublet state transition energies and oscillator strengths for the systems indicated. Adequate experimental data are available only for allyl$^\cdot$, benzyl$^\cdot$, butadiene$\overset{-}{\cdot}$, naphthalene$\overset{+}{\cdot}$, and naphthalene$\overset{-}{\cdot}$, together with fragmentary observations for styrene$\overset{-}{\cdot}$ and azulene$\overset{-}{\cdot}$, but the agree-

Table 1. *Comparison of experimental and calculated doublet state excitation energies*

	Calculated		Experimental	
	ΔE (eV)	f	ΔE (eV)	f
Ethylene$\overset{-}{\cdot}$, D_{2h}, ground state $^2B_{3g}$				
$^2B_{2u}(z)$	4.99	0.199		
Butadiene$\overset{-}{\cdot}$, C_{2h}, ground state ^2A_u				[a]
$^2B_g(x, y)$	2.15	0.068	2.17	weak
$^2B_g(x, y)$	3.59	0.539	3.19	med
Hexatriene$\overset{-}{\cdot}$, C_{2h}, ground state ^2B_g				
$^2A_u(x, y)$	1.56	0.129		
^2B_gforb.	2.92	0		
$^2A_u(x, y)$	2.95	0.836		
^2B_gforb.	4.46	0		
Octatetraene$\overset{-}{\cdot}$, C_{2h}, ground state ^2A_u				
$^2B_g(x, y)$	1.25	0.214		
^2A_uforb.	2.42	0		
$^2B_g(x, y)$	2.57	1.057		
$^2B_g(x, y)$	3.41	0.001		
^2A_uforb.	3.84	0		
^2A_uforb.	4.93	0		
$^2B_g(x, y)$	4.97	0.018		

Table 1 (continued)

	Calculated		Experimental	
	ΔE (eV)	f	ΔE (eV)	f
Decapentaene$^{\overset{-}{\cdot}}$, C_{2h}, ground state ^2B_g				
$^2A_u(x, y)$	1.01	0.323		
^2B_gforb.	2.07	0		
$^2A_u(x, y)$	2.32	1.192		
$^2A_u(x, y)$	3.02	0.002		
^2B_gforb.	3.41	0		
^2B_gforb.	3.75	0		
^2B_gforb.	4.37	0		
$^2A_u(x, y)$	4.45	0.026		
Styrene$^{\overset{-}{\cdot}}$, C_s, ground state $^2A''$				b
$^2A'(x, y)$	0.48	0.001		
$^2A'(x, y)$	1.76	0.155		
$^2A'(x, y)$	3.27	0.001		
$^2A'(x, y)$	3.60	0.479	3.35	med
$^2A'(x, y)$	4.38	0.076		
$^2A'(x, y)$	4.56	0.034		
Naphthalene$^{\overset{-}{\cdot}}$, D_{2h}, ground state $^2B_{2g}$				c, d, e
$^2B_{3g}$forb.	0.90	0	0.97	weak
$^2B_{1u}(x)$	1.69	0.112	1.64	0.290 (x)
$^2A_u(y)$	2.38	0.029	hidden	
$^2A_u(y)$	3.34	0.207	3.66	0.400 (y)
$^2B_{3g}$forb.	3.71	0		
$^2B_{1u}(x)$	4.40	0.164	3.83	0.370 (x)
$^2B_{1u}(x)$	4.87	0.436	4.23	med (x)
$^2B_{3g}$forb.	5.25	0		
$^2A_u(y)$	5.56	0.072	5.44	
Azulene$^{\overset{-}{\cdot}}$, C_{2v}, ground state $^2B_2$				f
$^2A_2(x)$	0.49	0.001		
$^2B_2(z)$	2.58	0.021		
$^2A_2(x)$	2.70	0.009	2.79	med
$^2B_2(z)$	3.00	0.016		
$^2B_2(z)$	3.37	0.003		
$^2A_2(x)$	3.76	0.023		
$^2B_2(z)$	3.79	0.036		
$^2A_2(x)$	4.60	0.114		
$^2B_2(z)$	4.63	1.583		
Naphthalene$^{\overset{+}{\cdot}}$, D_{2h}, ground state ^2A_u				g
$^2B_{1u}$forb.	0.78	0	spectrum virtually identical to that of naphthalene$^{\overset{-}{\cdot}}$	
$^2B_{3g}(x)$	1.49	0.096		
$^2B_{2g}(y)$	2.23	0.020		
$^2B_{2g}(y)$	3.13	0.196		
$^2B_{1u}$forb.	3.40	0		
$^2B_{3g}(x)$	4.18	0.257		
$^2B_{3g}(x)$	4.66	0.296		

Table 1 (continued)

	Calculated		Experimental	
	ΔE (eV)	f	ΔE (eV)	f
Azulene$^{\overset{+}{\cdot}}$, C_{2v}, ground state $^2A_2$				
$^2B_2(x)$	1.02	0.002		
$^2A_2(z)$	2.42	0.001		
$^2B_2(x)$	2.64	0.000		
$^2B_2(x)$	3.14	0.038		
$^2A_2(z)$	3.34	0.098		
$^2A_2(z)$	3.66	0.007		
$^2B_2(x)$	4.17	0.000		
$^2B_2(x)$	4.54	0.144		
$^2A_2(z)$	4.67	0.817		
Allyl$^{\cdot}$, C_{2v}, ground state $^2A_2$				[h,i]
$^2B_2(x)$	2.69	0.000	3.04	weak
$^2B_2(x)$	5.85	0.690	5.53	med
Pentadienyl$^{\cdot}$, C_{2v}, ground state $^2B_2$				
$^2A_2(x)$	1.84	0.000		
$^2B_2(z)$	3.30	0.000		
$^2A_2(x)$	4.66	1.242		
Heptatrienyl$^{\cdot}$, C_{2v}, ground state $^2A_2$				
$^2B_2(x)$	1.51	0.000		
$^2A_2(z)$	2.72	0.000		
$^2B_2(x)$	3.81	0.002		
$^2B_2(x)$	3.92	1.785		
Benzyl$^{\cdot}$, C_{2v}, ground state $^2B_2$				[j,k,l,m]
$^2A_2(x)$	2.65	0.000	2.70—2.85	weak
$^2B_2(z)$	2.87	0.000		
$^2A_2(x)$	3.77	0.074	3.97	med
$^2B_2(z)$	3.93	0.000		
$^2B_2(z)$	5.17	0.397	4.95	med

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ment is most satisfactory for a non-empirical calculation. Actually there are not even many semi-empirical treatments of open-shell systems, the only comprehensive account being that of Zahradnik and Carsky [15]. On the whole our agreement with experiment is slightly better than that achieved by these authors, but all our values parallel theirs very closely, encouraging us to believe that the non-empirical method can provide a reliable description of open-shell systems.

For naphthalene$^{\overset{-}{\cdot}}$ the low energy transitions are well reproduced, and although the bands at about 4 eV, are somewhat overestimated, the correct polarisations are predicted where these are known, and the peak at 5.44 eV is closely estimated. For naphthalene$^{\overset{+}{\cdot}}$ the experimental spectrum is almost identical with that of naphthalene$^{\overset{-}{\cdot}}$, as expected for an alternant hydrocarbon, and the calculated values, although consistently some 0.2 eV lower than those of the negative ion, parallel those of the latter very closely.

It seems reasonably well established that the free azulene$^{\overset{-}{\cdot}}$ anion is produced by polarographic reduction of azulene, this being accompanied by a disappearance

Table 2. *Composition of spectroscopic levels after full allowance for configuration interaction*

Spectroscopic level	Weights of contributing configurations (%) [a]
Hexatriene$^{\overset{-}{\cdot}}$	
Ground state	98.0, *G*; 0.9, C_β, (5–9); 0.4, C_β, (4–8).
1	81.6, *B*, (4–5); 14.5, *A*, (3–4); 2.2 C_β, (3–6).
2	76.9, *B*, (4–6); 11.4, C_β, (3–5); 10.1, *A*, (2–4).
3	74.6, *A*, (3–4); 13.7, *B*, (4–5); 7.1, C_β, (2–5).
4	56.5, *A*, (2–4); 14.3, *B*, (4–6); 9.7, C_β, (3–5).
Naphthalene$^{\overset{-}{\cdot}}$	
Ground state	97.0, *G*; 2.1, C_α, (3–5); 0.4, C_β, (2–6).
1	96.3, *B*, (6–7); 1.4, C_β, (4–9); 1.3, C_β, (2–7).
2	93.4, *B*, (6–8); 2.2 C_α, (5–7); 1.8, C_β, (5–10).
3	72.9, *B*, (6–9); 18.5, *A*, (5–6); 4.9, C_β, (4–7).
4	67.7, *A*, (5–6); 13.3, *B*, (6–9); 8.7, C_β, (4–7).
5	46.0, *B*, (6–10); 31.3, *A*, (3–6); 20.5, C_β, (5–8).
6	54.1, C_α, (5–7); 27.0, *A*, (4–6); 14.3, C_β, (5–7).
7	50.7, *A*, (4–6); 42.0, C_β, (5–7); 2.6, C_α, (5–7).
8	41.0, *A*, (3–6); 40.8, *B*, (6–10); 7.6, C_α, (5–8).
9	83.5, C_β, (4–7); 9.6, *B*, (6–9); 2.3, C_β, (4–10).
Benzyl$^{\cdot}$	
Ground state	96.0, *G*, 2.0, C_β, (2–6); 0.8, C_β, (3–5).
1	40.1, *A*, (3–4); 30.7, *B*, (4–5); 9.9, C_β, (3–6).
2	36.5, *A*, (2–4); 30.7, *B*, (4–6); 28.4, C_β, (2–6).
3	36.4, *B*, (4–5); 30.1, *A*, (3–4); 18.7, C_β, (2–5).
4	79.3, C_β, (3–5); 7.7, *A*, (1–4); 6.4, *B*, (4–7).
5	39.4, *A*, (2–4); 36.6, *B*, (4–6); 10.6, C_α, (2–6).

[a] Only the three most predominant configurations are listed.

of the characteristic blue absorption of the hydrocarbon and its replacement by a green colour showing one maximum at 445 mμ (2.79 eV), between 390 and 500 mμ. Our calculated spectrum is thus in good agreement since no band is predicted in the blue region, whilst three of moderate intensity are expected between 400 and 500 mμ.

For the benzyl radical our results predict the positions of the three main absorptions very well: the lowest $^2A_2$ and $^2B_2$ excited states, at 2.65 and 2.87 eV, are not symmetry forbidden but merely of very low ($< 1 \times 10^{-3}$) predicted intensity, and in fact coincide almost exactly with those found by flash photolysis. The other two main absorption regions are satisfactorily reproduced, and although the relative intensities are incorrectly estimated it is somewhat doubtful if the experimental peak heights are quantitatively reliable.

In Table 2 we list the weights of the excited state configurations which contribute to the calculated doublet transitions for three representative systems – hexatriene$^{\overset{-}{\cdot}}$, naphthalene$^{\overset{-}{\cdot}}$, and benzyl$^{\cdot}$. Our results clearly support the contention of Zahradnik and Carsky [15] that no meaningful interpretation of the spectra of open-shell systems is possible without extensive allowance for configuration interaction, and throughout the levels correspond to appreciably less pure states than for closed-shell molecules. Our excited states appear to be slightly purer than those of Zahradnik and Carsky, but this is probably because their results relate to the approximate Longuett-Higgins and Pople method and ours to the exact Roothaan treatment.

Ionisation Potentials and Electron Affinities

In Table 3 are listed the calculated ionisation potentials for the twelve systems studied, together with the available experimental values. We also give for comparison the results obtained by the empirical procedure of Part II [8], and these and the present results are also given for the pseudo-aromatic systems-fulvene, fulvalene, and heptafulvene. Considering that the values calculated by the non-empirical method represent only a small difference between two large quantities, the agreement with the experimental quantities is remarkably good, and the discrepancies do not exceed about 0.9 eV.

Also listed in Table 3 are the calculated electron affinities for the closed-shell systems, although there are very few experimental values for comparison. The experimental electron affinities are much smaller than the corresponding ionisation potentials and the calculation of these quantities from the difference in total energy between the hydrocarbon and its radical anion must be subject to appreciable error. The agreement found for azulene is thus surprisingly good, and although for naphthalene the calculated quantity is of incorrect sign the overall error is not great and other SCF treatments also lead to this result.

Table 3 also indicates that the ionisation potentials derived by the empirical method of Part II closely follow those obtained in the present work: this is true both for the twelve main systems studied and also for the three pseudo-aromatic molecules, thus supporting a cautious optimism as to the reliability of the latter values.

Table 3. *Comparison of calculated and experimental ionisation potentials and electron affinities*

	I. P.			E. A.	
	Calc.		Expt.	Calc.	Expt.
	Present	Part II			
Ethylene	11.03	—	10.56[a]	−2.39	—
Butadiene	8.92	9.29	9.18[b]	−0.50	—
Hexatriene	8.11	8.53	8.26[c, i]	0.18	—
Octatetraene	7.64	—	7.80[c, i]	0.54	—
Decapentaene	7.43	—	—	0.72	—
Styrene	8.29	8.72	8.86[d]	−0.26	—
Naphthalene	8.46	8.35	8.26[e]	−0.62	0.15
Azulene	6.80	7.47	7.72[f]	0.86	0.66
Allyl	9.04	—	8.16[g]	—	—
Pentadienyl	7.79	—	7.73[h]	—	—
Heptatrienyl	7.13	—	—	—	—
Benzyl	7.74	—	7.73[g]	—	—
Fulvene	7.75	8.54	—	1.68	—
Fulvalene	9.13	8.69	—	1.75	—
Heptafulvene	7.76	7.31	—	0.34	—

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[i] Adiabatic values.

Spin and Charge Densities

In Table 4 the total charge density and spin density distributions are given, together with the experimental hyperfine splitting constants, for the systems allyl$^{\cdot}$, benzyl$^{\cdot}$, butadiene$^{\dot{-}}$, naphthalene$^{\dot{\pm}}$, and azulene$^{\dot{\pm}}$. Excluding the results for azulene$^{\dot{+}}$, the simple McConnell relationship, $a_i = Q\,\varrho_{ii}$, affords an excellent correlation ($r = 0.978$) between the observed hyperfine splitting constants, a_i, and the calculated spin densities, with $Q = -23.32$ gauss. All positions with negative spin densities are correctly predicted, and the results for the non-alternant azulene$^{\dot{-}}$ radical are particularly satisfactory. It is interesting that the results for this system, and as a whole, do not suggest that any better correlation would be obtained by use of the two-parameter Colpa-Bolton equation, $a_i = (Q + K\varepsilon_i)\,\varrho_{ii}$, and, as noted by Tino [21], the Roothaan method appears particularly accurate for negative spin densities.

The only system for which the correct relative magnitudes for spin densities at all positions was not obtained was the benzyl radical; here, as in many SCF calculations (e.g. Tino [21]) the spin density at the 2-position is predicted slightly to exceed that at the 4-position, whereas experimentally the opposite is found.

Table 4. *Comparison of calculated spin densities and experimental hyperfine splitting constants*

Molecule and position	Charge Uncorr.	density Corr.	Spin density	a_H(gauss)
Allyl$^\cdot$				[a]
1–	1.0117	1.0110	+0.5756	–14.38
2–	0.9766	0.9780	–0.1514	+ 4.06
Benzyl$^\cdot$				[b]
1–	0.9784	0.9784	–0.0847	—
2–	1.0007	1.0006	+0.1774	– 5.10
3–	1.0005	1.0008	–0.0537	+ 1.60
4–	1.0007	1.0010	+0.1554	– 6.30
7–	1.0187	1.0183	+0.6824	–16.40
Butadiene$^{\cdot-}$				[c]
1–	1.3227	1.3192	+0.4280	– 7.62
2–	1.1773	1.1808	+0.0720	– 2.79
Naphthalene$^{\cdot-}$				[d]
1–	1.1564	1.1561	+0.2284	– 4.90
2–	1.0990	1.0993	+0.0416	– 1.83
9–	0.9892	0.9891	–0.0400	—
Azulene$^{\cdot-}$				[e]
1–	1.1445	1.1442	–0.0244	+ 0.27
2–	1.1511	1.1499	+0.1348	– 3.95
4–	1.0694	1.0696	+0.2138	– 6.22
5–	1.0666	1.0679	–0.0569	+ 1.34
6–	1.1401	1.1404	+0.3683	– 8.82
9–	1.0739	1.0733	+0.1166	—
Naphthalene$^{\cdot+}$				[f]
1–	0.8534	—	+0.2320	– 5.54
2–	0.9112	—	+0.0390	– 2.06
9–	0.9708	—	–0.0417	—
Azulene$^{\cdot+}$				[g, h]
1–	0.9189	—	+0.4053	10.65
2–	0.9366	—	–0.1005	1.52
4–	0.9166	—	–0.0070	0.38
5–	0.8565	—	+0.1081	4.15
6–	0.9097	—	+0.0586	1.12
9–	0.8849	—	+0.0146	—

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[h] Signs of a_i not established.

It is possible that this result may depend on the parameters assumed for the exocyclic carbon atom, although recently [23] evidence has been presented showing that non-uniformity of the bond lengths of the benzenoid ring could be responsible. However, program space did not permit us to test this by a VBO calculation.

Unlike the alternant hydrocarbon, naphthalene, the predicted spin density distributions for the positive and negative radical ions of azulene are remarkably different. This is because for the anion the open-shell is of b_2 symmetry, whilst for the cation it is of a_2 symmetry, with a nodal plane containing the long axis of the molecule. Recently [24] experimental confirmation of this prediction for azulene$^{\dot{+}}$ has been obtained, and although the sign of the a_i parameters was not unequivocably determined, the results are clearly in excellent accordance with the molecular orbital calculations. For naphthalene, within the restrictions of the ZDO approximation, the pairing theorem requires the same spin density distribution for both cation and anion, the open-shells being of a_u and b_{2g} symmetry respectively, which have the same nodal behaviour as regards the $C_9 - C_{10}$ bond axis. Orthogonalisation produces small departures from the Coulson-Rushbrooke theorem, but the spin density distributions are still almost identical.

Finally, we investigated the effect of the second order $G-A$ and $G-B$ configuration interaction on the spin densities. For allyl$^{\cdot}$ the only A and B excited states are precluded by symmetry from interaction with the C_β configuration, and in naphthalene$^{\dot{\pm}}$ the high symmetry leads to only one B or A type state respectively being able to contribute. Even for azulene$^{\dot{\pm}}$, with the lower C_{2v} symmetry, the numerous A and B type contributions are quite small, but clearly they cannot in general be ignored. Thus in butadiene$^{\dot{-}}$, and benzyl$^{\cdot}$ some of them are of the order of ± 0.02 and ± 0.04 respectively, and for pentadienyl$^{\cdot}$ the A and B contributions are sufficient to reverse the predictions concerning the relative magnitudes of the spin densities at positions 1 and 3. Consequently such interactions should always be included in spin density calculations and consideration of only C_β terms may lead to significant errors.

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