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AN ANALYSIS OF THE THROUGH-BOND INTERACTION USING THE LOCALIZED MOLECULAR ORBITALS—IV

LONG-RANGE PROTON HYPERFINE COUPLING IN EXO- AND ENDO-HYDROGENS IN BICYCLO[2.1.1]HEX-5-YL RADICAL

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Abstract—The INDO calculations were performed on bicyclo[2.1.1]hex-5-yl radical. From these calculations, it was confirmed that the hyperfine coupling constants depend largely on the geometry of the α hydrogen. The localized MO's were obtained from the canonical MO's calculated by using the INDO method. With the use of the localized MO's thus obtained, the variation in the hyperfine coupling constants at the 6*exo*- and 6*endo*-protons in this radical was explained in terms of the through-bond and/or the through-space interactions according to the procedure which we proposed previously. That is by the procedure we can selectively pick up a particular interaction between the specified localized MO's. The hyperfine coupling constant in this radical can be expressed by the summation of several interaction terms. The difference in the hyperfine spin coupling constants of the H_{6exo} and H_{6endo} in the radical now concerned has been attempted to explain using MO coefficients of the occupied orbitals.

Hyperfine spin coupling constants (hfsc's) of the 6*exo*- and 6*endo*-protons in bicyclo[2.1.1]hex-5-yl radical (**1**) have been determined previously.[1,2] In these papers,[1,2] the observed hfsc's are very different between the *exo*- and *endo*-protons. In other radicals also, the hfsc's have been found to have fairly different values between the *exo*- and *endo*-protons.[3-8] Hfsc's on the α, *exo*-, and *endo*-protons as a function of the angle α were already pursued by the semi-empirical method for bicyclo[1.1.0]-butyl radical.[9] Recently, Berthier *et al.*,[10] have carried out similar calculations for the same radical by using an *ab initio* SCF MO procedure. In that paper,[10] they have evaluated the contributions of the spin-delocalization term and the spin-polarization term to the total Fermi contact splitting, and they have proposed the condition that the W and anti-W rules can be applicable from the results of the calculations. The W-plan arrangement which is the empirical model to explain the large long-range hfsc have been studied previously.[11-14] In those papers, Ellinger *et al.*, have described the origin of the W and anti-W rules.[14] On the W hydrogen, spin-delocalization and spin-polarization contribute positively to the hfsc; this gives a large hfsc in the W arrangement. On the contrary, on the anti-W hydrogen, spin-delocalization and spin-polarization have opposite signs and the same order of magnitudes. Here in the radical **1**, H_{6exo} and H_{6endo} correspond to the anti-W and W arrangements respectively. The mechanism of the long-range spin coupling and the related works have been carried out theoretically and experimentally, and some models to explain the long-range couplings have been proposed.[15-24] The data upto 1975 have been reviewed very adequately by King.[25] However, the mechanism of the long-range hyperfine interactions seems not to be understood satisfactorily, and therefore a new approach will be required.

The long-range interaction between remote orbitals was first reported by Hoffmann *et al.*, in terms of the through-space and/or the through-bond interactions.[26,27] The ESR and NMR couplings are discussed in terms of the localized MO's using the double perturbation theory.[23] In that work the through-space and the through-bond concepts concerning the mechanism of the long-range coupling have been described, and the NMR proton-proton coupling has been analysed by some typical terms contributing to the coupling constants. However, the procedure has some difficulties in the treatment. We have previously proposed the very simple procedure to estimate quantitatively the effect of a particular through-bond or a through-space interaction between the remote orbitals.[28] This procedure has been successfully applied to explain the long-range hfsc's in bridgehead alkyl radicals: bicyclo[1.1.1]pent-1-yl bicyclo[2.1.1]hex-1-yl, and bicyclo[2.2.1]hept-1-yl radicals.[29] The procedure has also been applied to explain the lone-pair orbital interaction in azines,[30] and to explain the long-range effect of lone-pair orbital to optical rotatory strength of the carbonyl n $\rightarrow \pi^*$ transition in 3-ketopiperidines.[31] In the present work, we have attempted to explain the reason of largely different hfsc's between the *exo*- and *endo*-protons in **1** using the previously reported procedure. One of the main aspects of the present paper is, therefore, to examine the relation between the structural difference of *exo*- and *endo*-positions and the difference in their hfsc's in the light of the terminologies of the through-bond and through-space interactions by using the localized LMO's.

METHOD OF CALCULATIONS

The occupied α-spin orbitals were localized according to the method of Edmiston-Ruedenberg.[32] The virtual orbitals for the α-spin and all of the β-spin orbitals were not transformed into the LMO's. The orginal CMO's were obtained from the INDO calculations.[33] The localized α-spin orbitals were used as the basis in the SCF calculations both for α-and β-spin orbitals. Geometry used in the calculations was assumed to be identical with that of the parent alkane[34] except the coordinate of α-hydrogen. As for the α-hydrogen, the coordinates assumed at the angle $\alpha = 0°$ and the angle $\alpha = 34°$ were used. By using two kinds of the LMO's corresponding to two values for the angle α, we can study the difference in the long-range interaction courses owing to the difference in the angle α. Schematic structure and atom numbering of **1** are shown in Fig. 1. Here, the C5-H13 bond bent toward the *exo* direction is the case, $\alpha > 0°$.

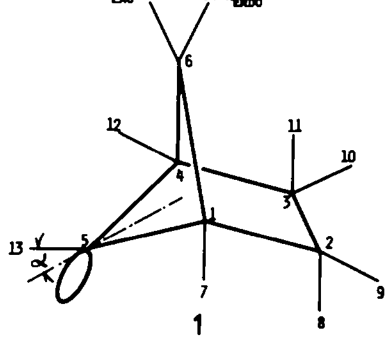

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Fig. 1. Schematic structure and atom numberings of bicyclo[2.1.1]hex-5-yl radical (**1**).

The detailed procedure for the analysis to estimate the effect of a particular through-bond or a through-space interaction has been described previously.[28,29] Therefore, the method is not reviewed in the present paper.

RESULTS AND DISCUSSION

Relation among α, total energy, and hfsc's. The total energy and hfsc's on H_α, H_{6exo}, and H_{6endo} as a function of α is shown in Fig. 2. The hfsc on H_α varies from the positive value to negative and again it becomes the positive value when the angle α changes from −60° to 60°. In this range, the hfsc of the H_{exo} varies scarcely, while that of the H_{endo} increases almost monotonously and continuously.

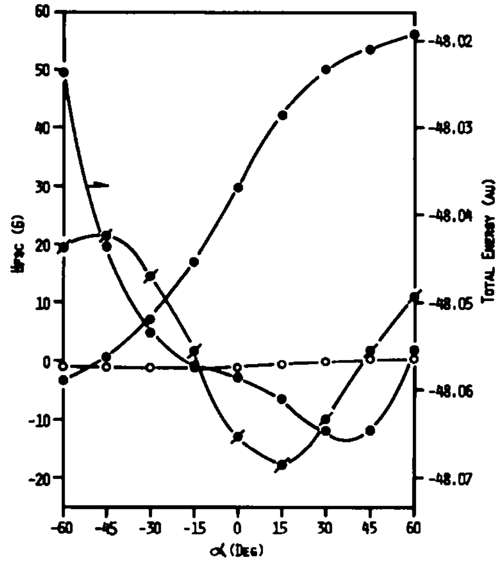


Fig. 2. Hfsc's and total energy as a function of angle α for bicyclo[2.1.1]hex-5-yl radical (**1**). —○—: H_{6exo}, —◐—: H_{6endo}, —Ø—: H_α (H13). —●—: total energy.

As for the total energy, the energy minimum appeared around $\alpha = 34°$. The calculated hfsc's at $\alpha = 34°$ reproduced fairly well the observed values,[2] although the observed values reported are the absolute ones. Therefore, the analysis of the long-range coupling has been carried out by the aid of the LMO which is transformed from the CMO calculated at $\alpha = 34°$, i.e., nearly sp^3 hybridization. In addition to the case of $\alpha = 34°$, the LMO, which is transformed from the CMO calculated at $\alpha = 0°$, i.e., nearly sp^2 hybridization is also used in the analysis.

Figure 3 shows the interaction diagrams of the long-range coupling with regard to H_{6exo} and H_{6endo} in **1**. Hfsc's in each corresponding interaction diagram are summarised in Table 1. Detailed analysis of the long-range proton hfsc in **1** is listed in Table 2.

The case of the angle $\alpha = 34°$. As for the H_{6exo} and H_{6endo}, it seems that the long-range interaction course between the odd electron and the protons concerned is very different with each other. With H_{exo}, the through-bond through-bond coupling, through-space via the long path, and the direct through-space are the dominant ones to govern the hfsc's. On the other hand, the through-space through-space coupling and the through-bond through-space coupling terms have negatively large values.

With H_{endo}, the dominant term to govern the hfsc's is the through-bond interaction term, and the term of the through-virtuals is the next largest. The direct through-space interaction is also one of the dominant terms. On the contrary, the terms of the through-bond through-space, through-space through-space couplings, and the through-space via the long path are the negative values.

The case of the angle $\alpha = 0°$. The CMO values (full interaction case) of the H_{exo} are not so different both in the cases of $\alpha = 34°$ and $\alpha = 0°$. On the

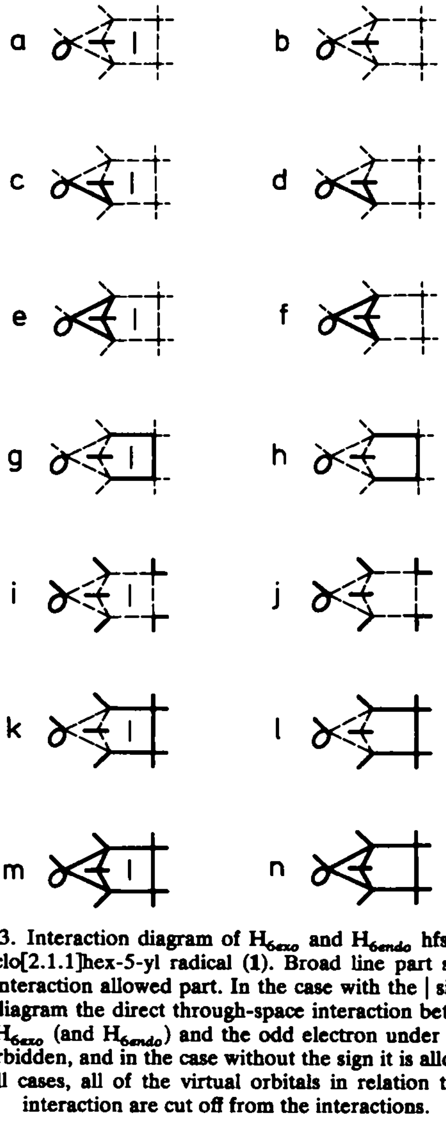


Fig. 3. Interaction diagram of H_{6exo} and H_{6endo} hfsc's in bicyclo[2.1.1]hex-5-yl radical (1). Broad line part shows the interaction allowed part. In the case with the | sign in the diagram the direct through-space interaction between the H_{6exo} (and H_{6endo}) and the odd electron under study is forbidden, and in the case without the sign it is allowed. In all cases, all of the virtual orbitals in relation to the interaction are cut off from the interactions.

contrary in the case of H_{endo}, the CMO value of the case of $\alpha = 34°$ is about 1.7 times larger than that of the $\alpha = 0°$. With H_{exo}, the term of the direct through-space is the dominant one in contrast with the case of $\alpha = 34°$. As for the H_{endo}, the largest term is the direct through-space interaction term, and the through-virtuals is the next largest. Here, the through-bond by single path in the case of $\alpha = 0°$ is much smaller than that in the case of $\alpha = 34°$.

The through-space via the long path and the through-virtuals have nearly equal values in both cases, $\alpha = 34°$ and $\alpha = 0°$. Therefore, it may be concluded that the contributions of these terms are not affected much by the variation of the angle α. The through-bond and the direct through-space terms are largely different with each other for the cases of $\alpha = 34°$ and $\alpha = 0°$. Therefore, in other words these two terms can decide most of the hfsc of H_{endo}. From these results, it should be stressed that the role of the direct through-space and the through-bond interactions for H_{endo} varied conclusively under the variation of the angle α. It is also very interesting that the through-space via the long path is positive in H_{exo} and on the other hand in H_{endo} it is negative in both cases of $\alpha = 34°$ and $\alpha = 0°$. Therefore, it should be recognizable that the mechanism of the long-range coupling between the radical center and the H_{exo} is very different from that between the radical center and the H_{endo}.

GENERAL DISCUSSION

One of the main aspects of the present work is to know the reason why the hfsc's of H_{exo} and H_{endo} are so different with each other. The difference of each interaction term in the hfsc's for H_{exo} and H_{endo} is briefly discussed in the preceding paragraph.

Now let us examine in more detail the through-bond interaction in the case of the angle $\alpha = 34°$. The diagram of the through-bond interaction is shown in Fig. 4. Through this through-bond interaction of the c state, the hfsc's become 0.04 and 21.13 G for H_{exo} and H_{endo}, respectively. This path can be subdivided into the three interactions as are shown in Fig. 4: one pure through-bond (o) and two indirect through-space interactions (p and q). When we have summed up the values of each interaction, they become almost the values of the above-mentioned through-bond interaction, that is, the c state. Therefore the additivity rule is approximately valid for the through-bond interaction. In conclusion, the mechanism of the through-bond path is reasonably explained.

Table 1. Hfsc's (G) of H_{6exo} and H_{6endo} in bicyclo[2.1.1]hex-5-yl radical (1)

	$\alpha=34°$		$\alpha=0°$			$\alpha=34°$		$\alpha=0°$	
a)	H_{exo}	H_{endo}	H_{exo}	H_{endo}	a)	H_{exo}	H_{endo}	H_{exo}	H_{endo}
a	-0.03	0.51	-0.05	-0.17	b	1.07	8.35	4.59	16.70
c	0.04	21.13	0.26	5.81	d	-1.17	31.60	0.41	26.44
e	1.85	43.95	1.55	13.60	f	-0.76	54.50	-0.96	38.43
g	1.42	-4.90	0.34	-5.62	h	-0.42	-2.08	1.30	6.47
i	0.30	6.00	-0.01	1.45	j	2.57	13.97	4.04	18.90
k	0.13	-3.01	0.59	-5.15	l	-0.31	1.43	0.86	8.09
m	4.25	22.62	7.08	-1.66	n	0.05	34.69	-0.95	16.22
CMO[b]	0.08	51.15	-1.15	29.59					

[a] See also Fig. 3. [b] Full interaction case.

Table 2. Analysis of H_{6exo} and H_{6endo} hfsc's (G) in bicyclo[2.1.1]hex-5-yl radical (1)

	$\alpha=34^\circ$		$\alpha=0^\circ$		Descriptions[a)]
	H_{exo}	H_{endo}	H_{exo}	H_{endo}	
Through-bond by single path (A)	0.07	20.62	0.31	5.98	c - a
Through-bond by two paths	1.88	43.44	1.60	13.77	e - a
Through-bond through-bond coupling (B)	1.74	2.20	0.98	1.81	(e - a) - 2(c - a)
Direct through-space (C)	1.10	7.84	4.64	16.87	b - a
Through-space via long path (D)	1.45	-5.41	0.39	-5.45	g - a
Through-space via C-H bonds (E)	0.33	5.49	0.04	1.62	i - a
Total through-space	-0.28	0.92	0.91	8.26	l - a
Through-space through-space coupling (F)	-3.16	-7.00	-4.16	-4.78	(l - a) - (C + D + E)
Through-bond through-space coupling (G)	-1.52	-10.18	-3.41	-5.64	(n - a) - [(e - a) + (l - a)]
Through-virtuals (H)	0.00	16.97	-0.25	13.20	CMO - (n - a)
Total (CMO)[b)]	0.08	51.15	-1.15	29.59	2A + B + C + D + E + F + G + H

[a)] See also Fig. 3 and Table 1. [b)] Full interaction case.

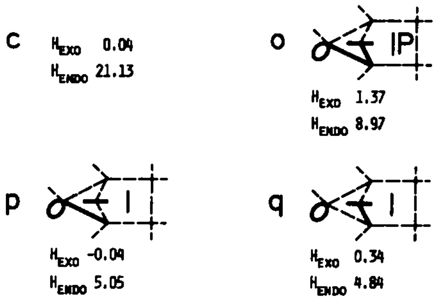
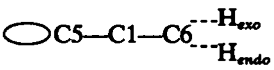


Fig. 4. Interaction diagram of H_{6exo} and H_{6endo} hfsc's in the through-bond path in bicyclo[2.1.1]hex-5-yl radical (1) ($\alpha = 34^\circ$). P (Pure through-bond interaction); only the through-bond interaction between the neighbouring bonds (orbitals) is allowed. In the state o, the interaction between the H_{6exo} and H_{6endo} is forbidden. In the other states, it is allowed. The other notations: see Fig. 3.

Why the hfsc's of H_{exo} and H_{endo} are so different? In the case of r, both H_{exo} and H_{endo} have very small calculated hfsc's (Fig. 5). In this case the odd electron can interact via the pure through-bond, but the path is interrupted at the bonds of C6-H_{exo} and C6-H_{endo}. In the case s, the odd electron on the C5 atom can interact with H_{exo} via the pure through-bond while in the state t, the odd electron on the C5 atom can interact with H_{endo} via the pure through-bond. In the t state, the calculated hfsc's are nearly equivalent to those of the o state. The situation of the bold line part



$$\bigcirc C5{-}C1{-}C6\begin{matrix}\cdots H_{exo}\\ \cdots H_{endo}\end{matrix}$$

is exactly the same both for the states t and s. Therefore, the difference between hfsc's of H_{exo} and H_{endo} may owe to the structural difference of H14 and H15 themselves. This is one of very important findings in the present work. In the case r, therefore, it may be said that the H_{endo} and H_{exo} are in the same interaction state as is expected. This situation is well explained by the calculated hfsc's. We have now taken up the cases r, s, and t, then the interaction mechanism would be examined. The electron densities for α- and β-spin electrons in these three cases are shown in the last column of Table 3.

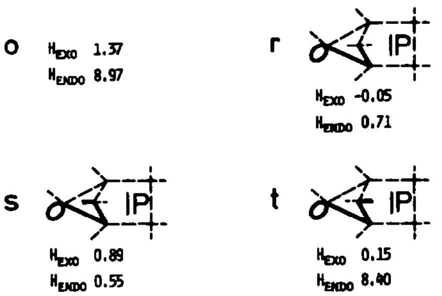


Fig. 5. Interaction diagram of H_{6exo} and H_{6endo} hfsc's in bicyclo[2.1.1]hex-5-yl radical (1) ($\alpha = 34^\circ$). In the state r, H_{6exo} and H_{6endo} are cut off from the interactions. Notations: see Figs. 3 and 4.

The difference in the electron density between α-and β-spins is the order of 0.015 in the case of "*endo*-through" (t), and in the cases of "*exo*-through" (s) and "both-cut" (r), those are in the order 0.001. Let us discuss the reason of these differences appearing. In Table 3, we have summarised the square of the MO coefficients in relation to the occupied orbitals relating to the H_{6exo} and H_{6endo}. From this table, it can be recognised that which orbital relates dominantly to the difference in the electron density. Here, the total difference of the electron densities between the α-and β-spins cannot be explained only by the difference in the electron density of MO's which have large MO coefficients on the radical center. That is, several orbital pairs govern the hfsc's of H_{exo} and H_{endo}. This finding corresponds well to the result that the strong couplings come from a cummulative effect of the delocalization and spin-polarization contributions.[10]

The coupling term relating to the long path. We

Table 3. Square of MO coefficients[e] of the occupied orbitals in relation to the H_{6exo} and H_{6endo} at the states[a] r, s and t in bicyclo[2.1.]hex-5-yl radical (1)

b)	r				s				t			
	H_{exo}		H_{endo}		H_{exo}		H_{endo}		H_{exo}		H_{endo}	
	α-spin	β-spin	α-spin	β-spin	α-spin	β-spin	α-spin	β-spin	α-spin	β-spin	α-spin	β-spin
1	0.001	0.001			0.001	0.001	0.027	0.027	0.001	0.001		
2			0.001	0.001					0.016	0.016	0.001	0.001
3			0.001	0.001	0.016	0.019					0.044	0.047
4							0.008	0.010	0.026	0.027		
5	0.001	0.001			0.002	0.002	0.115	0.115	0.101	0.113		0.001
6			0.002	0.002	0.004	0.003			0.002	0.004	0.001	0.001
7	0.003	0.002					0.005	0.002	0.005	0.001	0.003	
8	0.484	0.487	0.003	0.002	0.336	0.367	0.002	0.002	0.024	0.040	0.197	0.193
9	0.009	0.007	0.541	0.553	0.002	0.002	0.004	0.003	0.199	0.175	0.070	0.107
10	0.001	0.001	0.010	0.005	0.002	0.003	0.130	0.142	0.011	0.008		
11	0.005	0.005	0.008	0.003	0.127	0.108	0.012	0.004	c)	0.026	0.170[c]	0.001
12	0.004	0.005	0.002	0.002	0.001	0.007	0.045	0.051	0.024	0.069	0.006	0.005
13	0.001	0.001		0.001	0.002		0.069	0.062	0.068		0.001	0.202
14							0.002		0.003	0.002	0.001	0.001
15	0.001[c]	0.001	0.002[c]	0.002	0.019[c]		c)		0.020	0.027	0.009	0.002
16	0.001		0.004					0.140	0.008[c]		0.060[c]	
17		—		—	0.001	—	0.144	—	0.001	—	0.014	—
d)	0.511	0.512	0.573	0.571	0.513	0.511	0.559	0.558	0.508	0.508	0.576	0.560

[a] See Fig. 5. [b] Orbital number. [c] Orbital which is mainly relating to the radical center. [d] Electron density. [e] Values less than 0.001 are not cataloged.

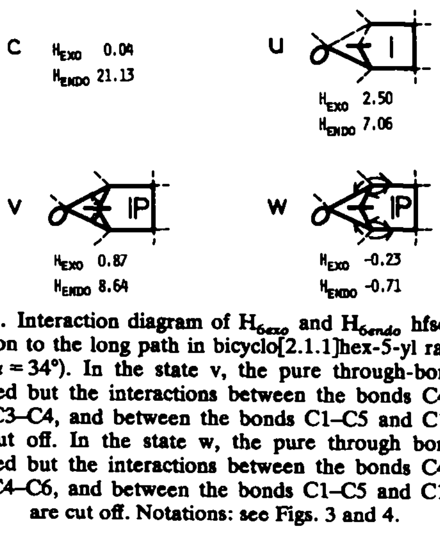


Fig. 6. Interaction diagram of H_{6exo} and H_{6endo} hfsc's in relation to the long path in bicyclo[2.1.1]hex-5-yl radical (**1**) ($\alpha = 34°$). In the state v, the pure through-bond is allowed but the interactions between the bonds C4–C5 and C3–C4, and between the bonds C1–C5 and C1–C2 are cut off. In the state w, the pure through bond is allowed but the interactions between the bonds C4–C5 and C4–C6, and between the bonds C1–C5 and C1–C6 are cut off. Notations: see Figs. 3 and 4.

have then discuss the case including the long path by using the Fig. 6. When we took up the cases c and u, the hfsc of the H_{exo} in the u state is larger than that of the c state, while the hfsc of the H_{endo} decreases largely by the addition of the long path. Now let us examine the states v and w. With the state v, the interaction between the odd electron and the H_{exo}/H_{endo} can be allowed by the pure through-bond path. The hfsc's of the H_{exo} and H_{endo} in this case are nearly equivalent to those of the case o. The interaction beween the odd electron and the H_{exo} and H_{endo} via the long path (pure through-bond) is, however, negligibly small (w). From these results, it should be recognisable that there are no particular courses via the long path with large interaction. Therefore, in the case including the long path the hfsc on H_{endo} is always small. The reason may be explained as follows: some part of the odd electron from the radical center localised on the C2 and C3 carbons when the interaction included the long path. This is also shown, for example, by fairly large hfsc's observed for H_{3exo} and H_{3endo} in bicyclo[2.2.1]hept-2-yl radical:[6] $H_{3exo} = 41.7$ and $H_{3endo} = 25.6$ G.

CONCLUDING REMARKS

The mechanism of the long-range hyperfine interactions has been examined in the light of the variation of the hfsc's of the H_{6exo} and H_{6endo} in bicyclo[2.1.1]hex-5-yl radical. The long-range interaction was then explained by several interaction terms: through-bond, through-space, through-virtuals, and some other coupling terms. The reason why the hfsc's of the H_{6exo} and H_{6endo} are so different has been examined by using the square of the MO coefficients of the occupied orbitals. From this we found that it is very difficult to explain the difference in the hfsc between H_{exo} and H_{endo} by only a pair of α- and β-orbitals. It may be concluded that, therefore, the difference in the hfsc between H_{6exo} and H_{6endo} in the radical considered may owe to the balance of the spin density of several orbital pairs.

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