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

LONG-RANGE PROTON HYPERFINE COUPLING 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

MASARU OHSAKU
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730, Japan

AKIRA IMAMURA and KIMIHIKO HIRAO
Department of Chemistry, Shiga University of Medical Science, Setatsukinowa-cho, Otsu, Shiga 520-21, Japan

and

TAKASHI KAWAMURA
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

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Abstract—The INDO calculations were performed on three 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. We have transformed the canonical molecular orbitals obtained by the INDO method into the localized molecular orbitals. With the use of the obtained localized molecular orbitals, the variation in the hyperfine coupling constant at the bridgehead proton in these radicals was pursued in terms of the through-bond (and/or the through-space) interaction according to the method by which we selectively can pick up a particular interaction between the specified localized molecular orbitals in a radical. As a result of this analysis, it was found that the hyperfine coupling constants in these radicals can be expressed by the summation of several terms; through-virtuals, through-space, through-bond, and some other coupling terms.

Hyperfine spin coupling constants (hfsc) of the bridgehead protons in bicyclo[2.1.1]hex-1-yl (2) and bicyclo[2.2.1]hept-1-yl (3) radicals (Fig. 1) have been estimated.[1,2] However, the observed hfsc of bicyclo[1.1.1]pent-1-yl radical (1) (Fig. 1) has not been published. The experimental and the theoretical aspects of the long-range coupling constants are also proposed on the other bridgehead alkyl,[3] azaalkyl[4] and haloalkyl radicals.[5] King has reviewed some of these radicals adequately.[6] Russell *et al.* have observed the long-range coupling in ESR spectra of semidiones.[7,8] With reference to these observations, the long-range hyperfine interactions have been explained by many authors.[6,9,10] The mechanism of the long-range spin coupling and the related works have been carried out theoretically and experimentally.[11–16] Recently a model to explain the hyperconjugation and through-space and through-bond interaction in the radicals now of interest has been proposed.[17] On the other hand, *ab initio* study of the short-range and long-range interactions in alkyl radicals have been reported.[18]

The long-range interaction between remote orbitals was first reported by Hoffmann *et al.* with the terminologies "through-space" and "through-bond" interactions.[19,20] To date, the explicit calculations of the through-bond interactions have not been carried out. In order to explain the spin coupling mechanism in the radicals studied, an attempt has been made to evaluate quantitatively the through-bond and/or the through-space interactions by using the localized molecular orbitals (LMO).

METHOD OF CALCULATIONS

The occupied α-spin orbitals were localized by the method of Edmiston–Ruedenberg.[21] The virtual orbitals for the α-spin and all of the β-spin orbitals were not transformed into the LMO. The original canonical molecular orbitals (CMO) were obtained from the INDO calculation.[22] The localized α-spin orbitals were used in actual calculations both for α- and β-spins. Geometries used for the radicals in the calculations were assumed identical with those of the parent alkanes[23–25] except the coordinates of the tervalent C atoms. These C atoms were shifted 0.1 Å inward the radicals.

The detailed analysis procedure to estimate the effect of a particular through-bond or a through-space interaction has been described in a previous paper.[26] The essential features of the method are reviewed briefly as follows.

We can represent a core resonance integral between atomic orbitals, χ_r and χ_s, as the summation of the core resonance integrals between the LMO, ψ_i and ψ_j,

$$I^0_{rs} = \sum_i \sum_j c_{ir} c_{js} I_{ij} \tag{1}$$

where I^0_{rs} and I_{ij} are the core resonance integral between the atomix orbitals, χ_r and χ_s, and that between the LMO, ψ_i and ψ_j, respectively. By modifying eqn (1), we can obtain the value of the core resonance integral between the atomic orbitals which gives zero for the core resonance integrals between the specified LMO, and gives the core resonance integrals between the other

LMO correctly. That is,

$$I_{rs} = I^0_{rs} - \sum_{(i_1-j_1)} (c_{i_1r}c_{j_1s} + c_{i_1s}c_{j_1r})I_{i_1j_1} \qquad (2)$$

where $(i_1 - j_1)$ means that the summation should cover over only definite pairs of the specified LMO. It is easily proved that the core resonance integrals, I_{rs}, by eqn (2) gives zero for the core resonance integrals between the specified LMO, $I_{i_1j_1}$, and the correct values for the others.

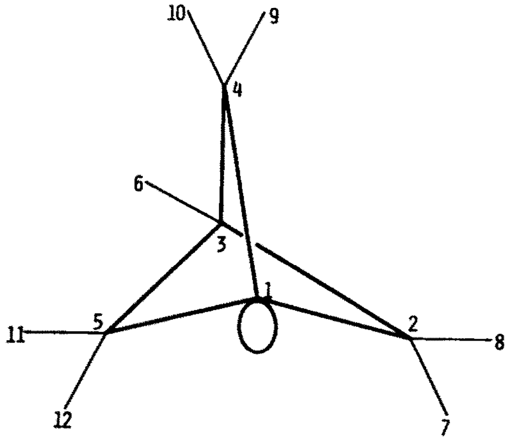
Consequently, when the LMO, ψ_i and ψ_j, which specified the bonds i and j, are picked up in eqn (2), for example, the core resonance integral between ψ_i and ψ_j should be cut off, that is, the through-bond interaction between the bonds i and j can be considered to be cut off.† Thus, the SCF calculations by using the core resonance integrals in eqn (2) give the hfsc without the relevant through-bond or the through-space interactions.

RESULTS

Figures 2–4 show the interaction diagrams of the long-range proton hfsc in 1, 2 and 3. Detailed analyses of the long-range proton hfsc in these radicals are summarized in Tables 1–3.

Bicyclo[1.1.1]*pent*-1-*yl radical* (1). There are four odd electron delocalization paths except via the virtual orbitals in this radical. With these four paths, we can divide them into one direct through-space and three through-bond interaction courses. As for the through-bond, all of the three paths are equivalent because of the geometry of this radical. The direct through-space interaction between bridgehead proton H_6 and an odd electron can be estimated from the difference in hfsc between the cases a and b shown in Fig. 2. With full interaction case (CMO), the hfsc of the proton H_6 is estimated as 83.93 G. Therefore, the role of the through-space interaction is not so dominant. The dominant one is the through-bond interaction. The through-bond interaction by three paths explains about 70% of the H_6 proton hfsc. Most of the rest is attributable to the interaction via the virtual orbitals as will be stated later.

Bicyclo[2.1.1]*hex*-1-*yl radical* (2). There are four main interaction courses except via the virtual orbitals; one direct through-space and three through-bond interactions. Two of these three through-bond paths are equivalent in this radical. The remainder is the long path. These have been named as "through-two-bond" or "through-three-bond", respectively.[17] In full interaction case (CMO), the calculated hfsc of the proton H_{11} is 24.14 G, and the observed value is estimated to be 22.49 G.[1] There seems to be good agreement between them. Now we can estimate the direct through-space interaction between bridgehead H_{11} and the odd electron from the values of the hfsc in the cases a and b of Fig. 3. The hfsc due to this direct through-space interaction is evaluated as 2.27 G. Therefore, it seems that this effect is not so large as to govern the hfsc in this radical. The



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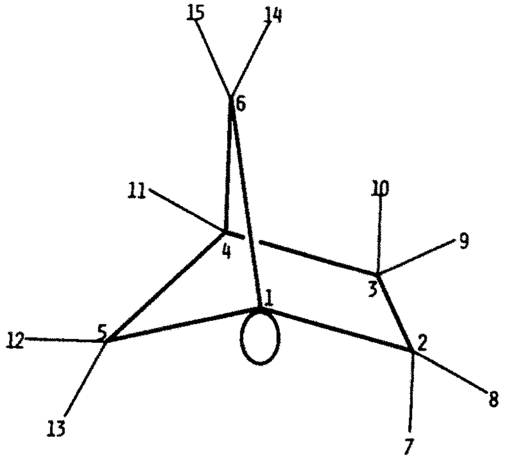

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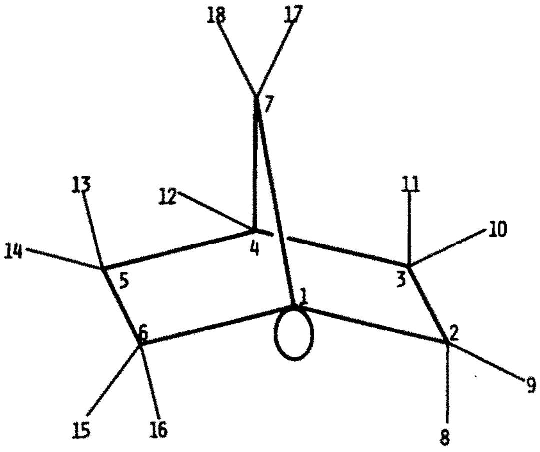

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Fig. 1. Schematic structures and atom numberings of bicyclo[1.1.1]pent-1-yl (1); bicyclo[2.1.1]hex-1-yl (2); bicyclo[2.2.1]hept-1-yl (3) radicals.

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†Strictly speaking, the through-space and the through-bond interactions defined in the present article do not include the exchange energy and include only the effect due to the core resonance integrals, whereas in the previous semi-empirical analysis[17] the through-space and/or the through-bond interactions are defined explicitly or implicitly including electrostatic interactions and even a part of the spin polarization effect. Although the through-space and the through-bond interactions involve usually the exchange energy, the through-bond interaction with the exchange energy is difficult to define by using the LMO, and moreover the problem treated in the present paper is not essentially affected by dropping the exchange energy in the definitions of the through-space and the through-bond interactions.

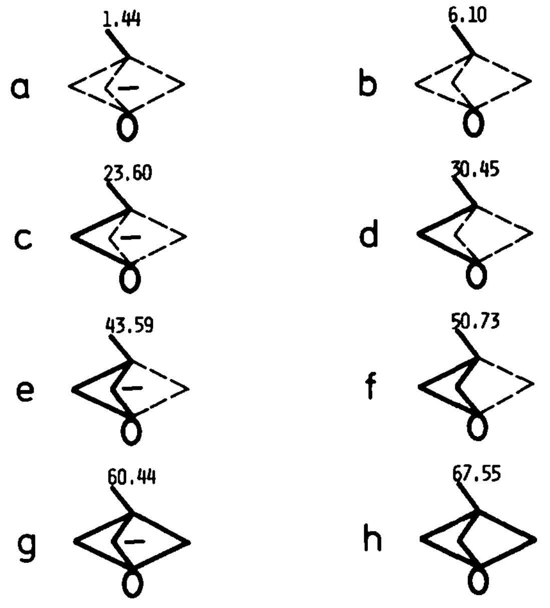

Fig. 2. Diagram of long-range proton hfsc (G) in bicyclo[1.1.1]pent-1-yl radical (1). Broad line part shows the interaction allowed part. C–H bonds in methylene groups are included on the line. In the case with — sign between bridgehead carbon atoms, the direct through-space interaction between the proton 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.

dominant factor to account for the hfsc in this radical is also seen in the through bond interaction as in the case of 1. To compare the role of the short and the long path, the short one has a much larger effect on the hfsc of the proton H_{11} than the long one.

Bicyclo[2.2.1]*hept*-1-*yl radical* (3). The observed hfsc on H_{12} is 2.45 G,[2] while the calculated value in full interaction case (CMO) is estimated to be 4.19 G. The present calculation reproduces the observed one fairly well. There are four interaction courses in this radical except via the virtual orbitals; one direct through-space and three through-bond paths. The direct through-space interaction in this radical is extremely small. Two long paths of this radical are equivalent. The short path has the largest effect of all on the hfsc, while the long path has little effect.

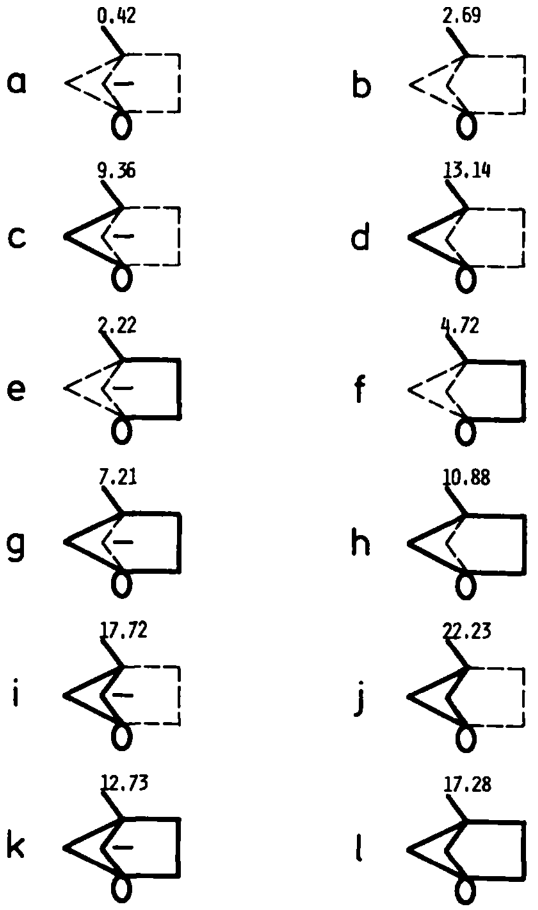

Fig. 3. Diagram of long-range proton hfsc (G) in bicyclo[2.1.1]hex-1-yl radical (2). Notations: see Fig. 2.

GENERAL DISCUSSION

The through-space interaction. The distance between bridgehead C atoms, and between the bridgehead carbon and the proton concerned are shown as follows together with the direct through-space hfsc of bridgehead protons.

	1	2	3
Distance between bridgehead carbon atoms, Å	1.74	2.07	2.23
Distance between bridgehead carbon and H, Å	2.84	3.18	3.26
Through-space hfsc (G)	4.66	2.27	0.59

Table 1. Analysis of long-range proton hfsc (G) in bicyclo[1.1.1]pent-1-yl radical (1)

	Hfsc	Descriptions[a]
Through-space (A)	4.66	b - a
Through-bond by a short path (B)	22.16	c - a
Through-bond by two short paths	42.15	e - a
Two short paths coupling (C)	-2.17	(e - a) - 2(c - a)
Through-bond by three short paths	59.00	g - a
Three short paths coupling (D)	-0.97	(g - a) - (3B + 3C)
Through-space and through bond coupling (E)	2.45	(h - a) - [(g - a) + (b - a)]
Through-virtuals (F)	17.82	CMO - (h - a)
Total (CMO)[b]	83.93	A + 3B + 3C + D + E + F

[a] See also Fig. 2. [b] Full interaction case.

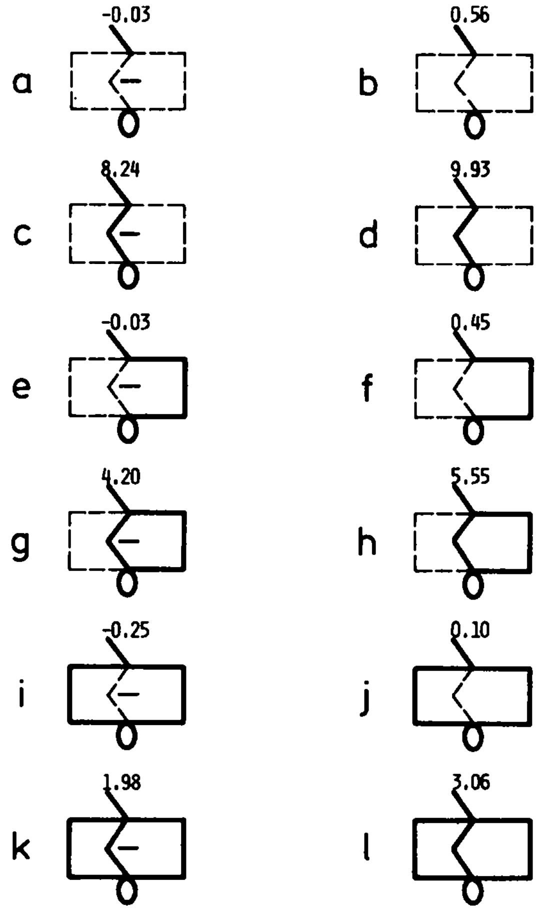

Fig. 4. Diagram of long-range proton hfsc (G) in bicyclo[2.2.1]hept-1-yl radical (3). Notations: see Fig. 2.

The direct through-space hfsc decreases with increase in distance. Therefore the through-space hfsc intimately relates to the distance between the bridgehead carbon or between the bridgehead carbon and the proton. However, the effect of the direct through space interaction on hfsc is smaller than the other terms in these radicals.

The through-bond interaction. There are two kinds of through-bond paths as stated in the preceding paragraph; the short path and the long path. Via the short path, the hfsc is greatly decreased from 1 to 2, and remains almost constant from 2 to 3. There is an empirical concept so-called "W-plan arrangement" to account for the stereoselectivity of the long-range coupling constants.[7-9] For example, a large γ coupling constant observed in bicyclo[2.2.2]oct-1-yl radical may also be mostly explained by the "short path" interaction.[3] This large interaction via the short path is attributable to the W-plan concept. With regards to the W-plan arrangement, Ellinger *et al.* have explained the strong long-range interaction in the γ position by a cumulative effect of spin delocalization and spin polarization.[10] The effect of this phenomena is partly explained by the present analysis.

The reason why the hfsc of the cases c is so different between for example, 1 and 2, in spite of the analogous short paths is not understood. We now discuss briefly by taking up the cases c of Figs. 2 and 3.

First, about 60% of odd electron (α-spin) still remains on the C_1 carbon after interaction in the case 2 as is summarized in Table 4. In the case of 1 only about 46% of it (α-spin) remains on C_1.

Second, as for the H atoms, the odd electron from C_1 almost localizes on H_6 in case 1. In the case 2, however, for example on H_{12} and H_{13} a part of the odd electron from C_1 appeared. For these reasons, as a result the hfsc is different in the short paths in 1 and 2. As for the long path, there seems to be no large difference between 2 and 3.

The role of coupling terms. For example the spin density on the bridgehead proton which appears via the two short paths does not become twice the value via the single short path. In the case of the long and the short paths, the calculated hfsc cannot be expressed by the sum of each that of the single path. The same is true in the case of three paths. We define here the difference between the calculated hfsc and the sum of the values for each path as the "coupling terms". The coupling therefore can also be defined between the through-bond and the through-space interactions.

We now consider the large coupling of "a short and a

Table 2. Analysis of long-range proton hfsc (G) in bicyclo[2.1.1]hex-1-yl radical (2)

	Hfsc	Descriptions[a]
Through-space (A)	2.27	b - a
Through-bond by a short path (B)	8.94	c - a
Through-bond by a long path (C)	1.80	e - a
Through-bond by a short and a long paths	6.79	g - a
A short and a long paths coupling (D)	-3.95	(g - a) - [(c - a) + (e - a)]
Through-bond by two short paths	17.30	i - a
Two short paths coupling (E)	-0.58	(i - a) - 2(c - a)
Through-bond by two short and a long paths	12.31	k - a
Three paths coupling (F)	1.11	(k - a) - (2B + C + 2D + E)
Through-space and through bond coupling (G)	2.28	(l - a) - [(k - a) + (b - a)]
Through-virtuals (H)	7.28	CMO - (l - a)
Total (CMO)[b]	24.14	A + 2B + C + 2D + E + F + G + H

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

Table 3. Analysis of long-range proton hfsc (G) in bicyclo[2.2.1]hept-1-yl radical (3)

	Hfsc	Descriptions[a]
Through-space (A)	0.59	b - a
Through-bond by a short path (B)	8.27	c - a
Through-bond by a long path (C)	0.00	e - a
Through-bond by a short and a long paths	4.23	g - a
A short and a long paths coupling (D)	-4.04	(g - a) - [(c - a) + (e - a)]
Through-bond by two long paths	-0.22	i - a
Two long paths coupling (E)	-0.22	(i - a) - 2(e - a)
Through-bond by two long and a short paths	2.01	k - a
Three paths coupling (F)	2.04	(k - a) - (B + 2C + 2D + E)
Through-space and through-bond coupling (G)	0.49	(l - a) - [(k - a) + (b - a)]
Through-virtuals (H)	1.10	CMO - (l - a)
Total (CMO)[b]	4.19	A + B + 2C + 2D + E + F + G + H

a See also Fig. 4. b Full interaction case.

Table 4. Frontier electron densities in HOMO (α-spin) and in LUMO (β-spin) in the cases[a] c of bicyclo[1.1.1]pent-1-yl (1) and bicyclo[2.1.1]hex-1-yl (2) radicals[b]

	1		2	
	α-spin	β-spin	α-spin	β-spin
Spin density on C_1	0.4623	0.7318	0.5984	0.8075
Spin density on H_6 (1) or H_{11} (2)	0.0891	0.0451	0.0425	0.0225
Spin density on H_{11} (1) or H_{12} (2)	0.0002	0.0000	0.0096	0.0052
Spin density on H_{12} (1) or H_{13} (2)	0.0002	0.0000	0.0068	0.0063

a See also Figs. 2 and 3. b See also Fig. 1.

long path". This term has a fairly large minus value,† and these coupling terms in 2 and 3 are nearly equal. This coupling is almost twice the two paths coupling in 1. From these we can deduce immediately that the hfsc of the proton under study in radicals which have the long path is expected always to be smaller in value than in radicals consisting only of the short path.

The role of virtual orbitals. The odd electron on the bridgehead proton which appears via the virtual orbitals gives 17.82, 7.28 and 1.10 G of hfsc in 1, 2, 3 respectively. These values are equal to 21%, 30% and 26% of the values with full interaction case, respectively. From these we can easily recognize that the spin density which appears on H concerned via the virtual orbitals are less dominant than that via the occupied orbitals. However, the role of the virtual orbitals is indispensable in the analysis of the long-range coupling in these radicals. Colpa *et al.* have described that the anti-bonding orbital cannot be neglected to estimate the spin densities on the aliphatic protons.[11] This result coincides well with our result, although the straightforward comparison between them has some difficulties.

In the present paper, however, we cannot obtain a definite image of the "couplings". For this reason, further analyses of the through-space and the through-bond interactions in these radicals and in the other radicals are needed. Such an attempt will be published in the near future.

CONCLUDING REMARKS

The mechanism of the long-range interaction between the odd electron and the bridgehead proton has been analysed quantitatively. The long-range interaction was divided into several terms, which were assigned to through-space, through-bond, through-virtuals, and coupling terms. Among them the dominant term via the occupied orbitals is the through-bond interaction via the short path in all radicals now concerned. The contribution of the through-virtual term is also one of the dominant terms.

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†This was referred as countering phase effect between the through-two-bond and the through-three-bond interactions in the previous analysis.[17]

REFERENCES

[1] T. Kawamura and T. Yonezawa, *J. Chem. Soc.* Chem. Commun. 948 (1976).

[2] T. Kawamura, M. Matsunaga and T. Yonezawa, *J. Am. Chem. Soc.* **97**, 3234 (1975).

[3] P. J. Krusic, T. A. Rettig and P. v. R. Schleyer, *Ibid.* **94**, 995 (1972).

[4] W. C. Danen and R. C. Rickard, *Ibid.* **97**, 2303 (1975).

[5] D. E. Wood, W. F. Bailey, K. B. Wiberg and W. E. Pratt, *Ibid.* **99**, 268 (1977).

[6] F. M. King, *Chem. Rev.* **76**, 157 (1976).

[7] G. A. Russell and K.-Y. Chang, *J. Am. Chem. Soc.* **87**, 4381 (1965).

[8] G. A. Russell, K.-Y. Chang and C. W. Jefford, *Ibid.* **87**, 4383 (1965).

[9] G. A. Russell, J. J. McDonnell, P. R. Whittle, R. S. Givens and R. G. Keske, *Ibid.* **93**, 1452 (1971).

[10] Y. Ellinger, A. Rassat, R. Subra and G. Berthier, *Ibid.* **95**, 2372 (1973).

[11] J. P. Colpa and E. de Boer, *Mol. Phy.* **7**, 333 (1964).

[12] J. P. Colpa, E. de Boer, D. Lazdins and M. Karplus, *J. Chem. Phys.* **47**, 3098 (1967).

[13] H. E. Zimmerman and R. D. McKelvey, *J. Am. Chem. Soc.* **93**, 3638 (1971).

[14] F. Gerson, R. Gleiter, G. Moshuk and A. S. Dreiding, *Ibid.* **94**, 2919 (1972).

[15] G. R. Underwood, V. L. Vogel and J. Iorio, *Mol. Phys.* **25**, 1093 (1973).

[16] F. W. King and F. C. Adam, *Ibid.* **29**, 337 (1975).

[17] T. Kawamura, M. Matsunaga and T. Yonezawa, *J. Am. Chem. Soc.* **100**, 92 (1978).

[18] Y. Ellinger, R. Subra, B. Levey, P. Mille and G. Berthier, *J. Chem. Phys.* **62**, 10 (1975).

[19] R. Hoffmann, A. Imamura and W. J. Hehre, *J. Am. Chem. Soc.* **90**, 1499 (1968).

[20] R. Hoffmann, *Acc. Chem. Res.* **4**, 1 (1971).

[21] C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.* **35**, 457 (1963).

[22] J. A. Pople, D. L. Beveridge and P. A. Dobosh, *J. Chem. Phys.* **47**, 2026 (1967).

[23] J. F. Chiang and S. H. Bauer, *J. Am. Chem. Soc.* **92**, 1614 (1970).

[24] J. F. Chiang, *Ibid.* **93**, 5044 (1971).

[25] J. F. Chiang, C. F. Wilcox, Jr. and S. H. Bauer, *Ibid.* **90**, 3149 (1968).

[26] Part I of this series: M. Ohsaku, A. Imamura and K. Hirao, *Bull. Chem. Soc. Jpn* **51**, 3443 (1978).