2986 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (11), 2986—2990 (1977) [Vol. 50, No. 11

Restricted Rotation Involving the Tetrahedral Carbon. XX. Barriers to Rotation and ^{13}C NMR Spectra of 9-(2-Alkylphenyl)fluorene Derivatives[1,2]

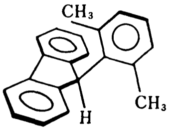
Mikio Nakamura,[3] Nobuo Nakamura, and Michinori Ōki*

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

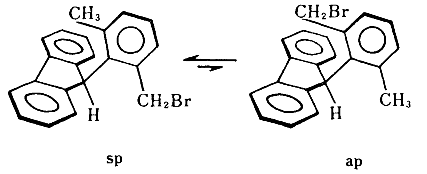
(Received June 22, 1977)

A series of 9-(2-alkylphenyl)fluorene derivatives are prepared and their internal rotation about the C_9–C_{ar} bond is examined. Those which have a methyl, an ethyl, or an isopropyl group in 2′ position exist as a mixture of sp and ap forms, showing coalescence phenomena in the NMR spectra at high temperatures. The barriers to rotation of these compounds are obtained by the usual DNMR method. 9-(2-*t*-Butylphenyl)fluorene, in contrast, is found to exsist exclusively as an sp form and thus the barrier to rotation must be determined by measuring the rates of conversion from the unstable ap form which is successfully obtained by the protonation of the corresponding lithium fluorenide at low temperatures. The barriers to rotation of the compounds are alike except for the *t*-butyl compound. The difference is explained in terms of the conformation of the alkyl group in the ground and the transition state for rotation. The ^{13}C NMR data also exhibit a large steric interaction between the alkyl group and the fluorene ring.

Barriers to rotation about C_9–C_{ar} bond are known to be extremely high in 9-arylfluorenes, especially when the aryl group is a 2,6-disubstituted phenyl.[4] For example, the barrier to rotation of 9-(2,6-dimethylphenyl)fluorene (**1**) was reported to be larger than 23 kcal/mol and, as expected from the barrier, we could isolate the two rotamers of structurally anologous 9-(2-bromomethyl-6-methylphenyl)fluorene (**2**). When one of the substituents in 2 and 6 positions of the aryl group is replaced by hydrogen, the barrier to rotation decreases to a great extent and the rotamer is no longer isolable at room temperature. In such a case DNMR method may become a powerful tool for deciding the barriers to rotation. The barrier to rotation of 9-(*o*-tolyl)-fluorene was measured to be *ca.* 16 kcal/mol by this method.[5]

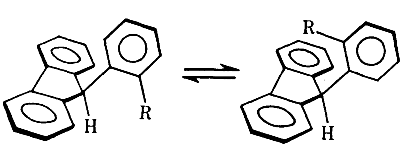


(**1**)



(**2**)

As for the equilibrium constant between rotamers, it depends mainly on the relative bulkiness of the substituents in 2 and 6 positions of the aryl, though in some cases electronic effect such as charge transfer stabilization controls the population.[1] Judging from the results on equilibrium constants, so far reported, in this series, a bulkier substituent is apt to take the position in proximity of 9-H. Thus, in the case of **2** the sp form is favored over the ap form as the bromomethyl is larger than the methyl group. If one of the substituents is exceedingly large, the populations of two rotamers must be one-sided. In such a case, information on the barrier to rotation cannot be obtained by the DNMR method. Signals due to the unfavorable ap forms of 9-(2-alkylphenyl)fluorene derivatives **4**, **5**, and **6** could be observed in the ^{1}H NMR spectra, whereas none of the signals attributable to the ap form could be detected when the substituent was *t*-butyl.[2] Thus compounds **4**, **5**, and **6** belong to a category which gives barriers to rotation by the DNMR method, whereas compound **7** needs a device for measuring the barrier. We could solve the latter problem by finding a method for preparing unstable isomer and by measuring the rates of isomerization.

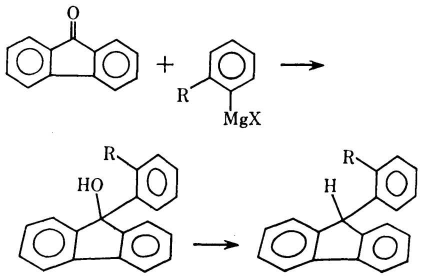


(**3**) R=H
(**4**) R=Me
(**5**) R=Et
(**6**) R=^{i}Pr
(**7**) R=^{t}Bu

In this paper we wish to describe the method for obtaining the barrier to rotation of 9-(2-*t*-butylphenyl)-fluorene (**7**) together with the substituent effects on the rotational barriers in the 9-(2-alkylphenyl)fluorene series. To identify the substituent, the positions are referred to by numbers with primes when they are carried in the 9-aryl group.

Experimental

Materials. The syntheses of 9-aryl-9-fluorenol were carried out by the Grignard reaction of fluorenone with the corresponding arylmagnesium halide followed by treatment with dilute hydrochloric acid. 9-Arylfluorenes were obtained by reducing the corresponding fluorenol with hydriodic acid. Details of the syntheses were described in a previous paper, taking **6** and **7** as examples.[6]



9-(2-Ethylphenyl)-2-fluorenol (10), mp 133—134 °C. Yield 75%. ^{1}H NMR ($CDCl_3$, δ): 0.43 (CH_3CH_2), 1.72 (CH_3-CH_2), 8.2 (6′-H). Found: C, 88.10; H, 6.36%. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34%.

9-(2-Ethylphenyl)fluorene (4), mp 65—66 °C. Yield 84%. ^{1}H NMR ($CDCl_3$, δ): 1.42 (sp-CH_3CH_2), 0.40 (ap-CH_3CH_2), 3.07 (sp-CH_3CH_2), 1.4 (ap-CH_3CH_2), 5.37 (sp-9-H), 4.95 (ap-9-H), 6.33 (sp-6′-H). Found: C, 93.45; H, 6.65%. Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.71%.

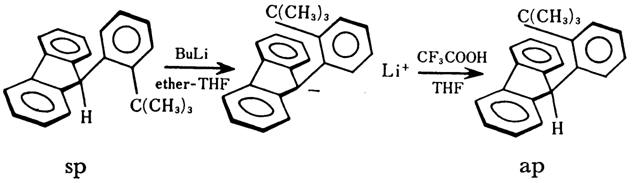
Table 1. Activation parameters for rotation and equilibrium constants at 0 °C

	sp→ap			ap→sp			K(ap/sp)
	ΔH^* (kcal/mol)	ΔS^* (eu)	ΔG^* (kcal/mol)	ΔH^* (kcal/mol)	ΔS^* (eu)	ΔG^* (kcal/mol)	
H[a)]	—	—	<9	—	—	<9	—
Me	15.9	−2.4	16.6	15.9	−1.5	16.3	1/1.6
Et	18.2	1.1	17.9	18.2	3.3	17.3	1/3.3
^{i}Pr	16.0	−8.6	18.3	16.0	−7.3	18.0	1/2.4
^{t}Bu	—	—	>23	21.8	5.6	20.3	<1/100

a) Data reported by Siddall *et al.*[5)] for 9-(*m*-tolyl)fluorene.

Synthesis of ap Form of **7**. The synthesis of thermodynamically unstable ap form of **7** was carried out by the following procedure.

To an NMR sample tube containing *ca.* 20 mg of **7** was added *ca.* 0.2 ml of ether–THF solution of butyllithium which contained about 0.15 mmol of net butyllithium. The solution gradually changed red as lithium salt was produced. When the 9-H signal disappeared completely, the sample was cooled to *ca.* −50 °C and a small amount of pre-cooled trifluoroacetic acid in THF was added in small portions with stirring until the solution turned colorless. The ^{1}H NMR spectra of the colorless solution showed the presence of only ap form at this temperature.



Kinetics. Although the ap form of **7** was stable at −50 °C, new signals assigned to the sp form appeared gradually when the temperature was raised up to *ca.* −10 °C. The rate of isomerization was followed by comparison of the signal height of 9-H's of two rotamers. The temperature was calibrated by the peak separation of methyl alcohol. Plots of log (1—*x*/*a*) *vs.* time gave a straight line and the first order rate constants were obtained by the usual way. The rate constants were $3.9\times10^{-4}\,s^{-1}$ (−1 °C), $1.2\times10^{-4}\,s^{-1}$ (−9 °C), and $4.1\times10^{-5}\,s^{-1}$ (−15 °C). Putting these rate constants into Eyring's equation, we could obtain the activation parameters for rotation.

As for compounds **4**, **5**, and **6**, barriers to rotation were obtained by the usual DMNR method since the signals of these compounds broadened and showed coalescence phenomena when the temperature was changed. Thus the rate constant at each temperature was obtained by the computer simulation of the observed curves. Free energies, enthalpies, and entropies of activation for rotation are given in Table 1 together with the equilibrium constants between rotamers.

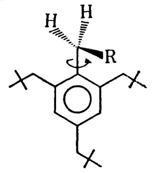
NMR Measurement. ^{1}H NMR spectra were determined on a Hitachi R-20B spectrometer operating at 60 MHz. ^{13}C NMR spectra were measured on a JNM-FX 60 spectrometer operating at 15.04 MHz and ^{13}C-^{1}H coupling constants were obtained from all proton undecoupled spectra. The estimated error in reading the coupling constants was ±0.5 Hz. In every compound except **7** the chemical shifts and the coupling constants of 9-C's of two rotamers were easily obtained since these compounds existed as a mixture of sp and ap form at the equilibrium. The ^{13}C NMR parameters of the ap form of compound **7**, on the other hand, was difficult to obtain as it was prepared by the protonation of the corresponding fluorenide anion at low temperature in ether–THF solution: These solvents interfered the measurement of the 9-C signal. Thus the solvent had to be replaced by $CDCl_3$. The replacement of the solvent was easily attained, since the 9-lithio derivative crystallized when the solution was maintained at −5 °C for a day. The solvents were decanted and the red crystals of the lithium salt were dried under reduced pressure. A $CDCl_3$ solution containing a small amount of trifluoroacetic acid was added slowly at −50 °C to the crystals placed in a ^{13}C NMR sample tube. After the solution was stirred vigorously, the ^{13}C NMR spectra were measured at −40 °C to exhibit a clear 9-C signal. These data are listed in Table 2.

Results and Discussion

Barriers to Rotation. In Table 1, kinetic parameters for rotation of compounds **4**, **5**, and **6** at 0 °C are listed for both sp→ap and ap→sp processes. We limit our discussion here on free energies of activation, since values of entropies of activation obtained by the DNMR method are often controversial.

The free energy of activation for the process sp→ap of compound **7** was not possible to obtain, since no *t*-butyl signal of the ap form could be detected at the equilibrium state. Although the extremely concentrated solution of **7** was prepared in order to observe the *t*-butyl signal of the ap form, if any, in ^{1}H NMR spectrum, no signal could be detected at the expected position. Thus we concluded that the equilibrium constant at 0 °C is less than 1/100 which corresponds to the free energy difference of *ca.* 2.5 kcal/mol. Since the barrier to rotation was estimated at 20.3 kcal/mol for the ap→sp process, that for sp→ ap must be larger than 23 kcal/mol from the above discussion. The measurement of the ^{1}H NMR spectrum at high temperature may be another possible method for detecting the ap form, since, in general, the population of a less stable isomer increases as the temperature is raised. But neither broadening of the *t*-butyl signal due to exchange nor the change of its chemical shift was observed up to 180 °C, indicating that the sp form is more stable than the ap form at least by *ca.* 2.5 kcal/mol even at 180 °C.

To start, let us compare the barriers to rotation for the process from the sp to the ap form. Data in Table 1 indicate that a considerably large increase in energy is observed when a methyl group is introduced in 2′ position in place of a hydrogen (more than 7 kcal/mol) and when an isopropyl group is replaced by a *t*-butyl group (more than 5 kcal/mol). In contrast to these the replacement of the methyl group by a bulkier ethyl or isopropyl group results in a small increase in activation energy. The substituent effect on the rotational barriers observed in this system is somewhat similar to that of neopentyl derivatives (**8**) reported by Dahlberg *et al.*;[7] barriers to rotation at the coalescence temperature are 10.6 (T_c=−56 °C), 10.7 (−53 °C), and 12.7 (−15 °C) kcal/mol for **8a**, **8b**, and **8c**, respectively, whereas it becomes as high as 17.6 kcal/mol (+82 °C) when R is a *t*-butyl.



8 **a** R=Me
b R=Et
c R=^{i}Pr
d R=^{t}Bu

In principle, the barriers to rotation are relative values: even if the absolute value of a barrier is very high, the barrier may be low if the ground state is rich in energy. We must, therefore, discuss both the transition state and the ground state, if we compare the barriers.

The transition state for rotation may be considered as a conformation which gives rise to most repulsive interaction between the alkyl group in 2′-position and 1 (or 8)-position of the fluorene ring, whereas the ground state involves the interaction of the alkyl group with 9-H. The fact that substitution of 2′-hydrogen by a methyl group causes great enhancement of the barrier is interpreted as such that the destabilization of the ground state due to 2′-CH_3–9-H interaction is relatively small and that of the transition state due to 2′-CH_3–1(or 8)-H is large.

Ground state of compounds **4**, **5**, and **6** may not differ to a great extent, because they can take a conformation in which the smallest group comes to a most crowded site. This type of consideration is well documented in explaining the free energy difference of axial-equatorial alkylcyclohexanes. Likewise the destabilization of the transition state will be also comparable for compounds **4**, **5**, and **6** (Fig. 1a). Thus the similar free energies of activation for rotation is reasonable, if the substituent in 2′-position has at least a hydrogen in α-position of the alkyl group, although the entropy factor may be unfavorable for those which have smaller number of hydrogens.

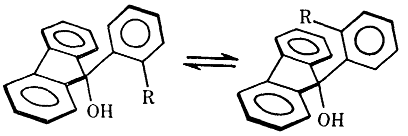
The *t*-butyl compound has no hydrogen to lessen the repulsion by taking a conformation of the least strain. Thus both the ground state and the transition state are greatly destabilized relative to the lower homologs. Again the effect seems to be larger in the transition state than in the ground state. Thus the barrier is increased to a great extent, compared to that of the isopropyl compound.

(a) Transition state (b) Ground state

Fig. 1. Possible conformations of the compound, the substituent of which has an α hydrogen.

The barriers to rotation of the ap→sp processes show a quite different aspect in a sense that only a 2 kcal/mol increase in energy is observed by the introduction of a *t*-butyl group instead of an isopropyl group. This clearly means that, in compound **7**, a remarkable amount of energy increase in the transition state for rotation is compensated by nearly the same degree of increase in energy in the ground state. The destabilization of the ap form of compound **7** can again be explained by taking the conformation of the alkyl group into account. In methyl, ethyl, and isopropyl derivatives the repulsive interaction between the substituent and the fluorene ring may not become so large if the α-hydrogen of the substituent faces the fluorene ring. Whereas in the *t*-butyl derivative severe repulsion inevitably occurs (Fig. 1b).

The large repulsion between the *t*-butyl group and the fluorene ring is more clearly demonstrated in 9-(2-alkylphenyl)-9-fluorenols **9**, **10**, **11**, and **12**. The ^{1}H NMR spectrum of compound **9** showed a characteristic feature of the ap form: a methyl signal appeared at a high field (δ 1.27) and 6′-H multiplet at a low field (δ 8.2). The ^{1}H NMR spectra of **10** and **11** showed the same trends as that of **9**, indicating that these compounds also existed as ap forms probably because of a large repulsion between the alkyl and the 9-hydroxyl groups compared with that between the alkyl group and the fluorene ring. The *t*-butyl derivative (**12**), on the other hand, was concluded to exist exclusively as the sp form, since the *t*-butyl signal appeared at a low field (δ 1.79) as a little broad singlet and signals due to 6′-H was observed at quite a high field (δ 6.4) also as a broad doublet. When the temperature was raised, the *t*-butyl signal showed further broadening and at 50 °C its half band width amounted to 2.9 Hz. The signals of 6′-H changed more appreciably in the same temperature range: the doublet broadened with the increase in temperature and at 60 °C the fine structure of the signals almost disappeared. Both signals sharpened on further raising of the temperature. When the temperature was lowered, there appeared a trace of a signal at δ 0.7 which was assigned to the *t*-butyl group of the ap form because structurally analogous **11** gave isopropyl signals of the ap form at δ 0.5. While it was difficult to obtain an accurate equilibrium constant from the spectra, it was roughly estimated to be 1/80 at −30 °C from the integration of the two signals. These results again suggest the existence of considerably large repulsion between the *t*-butyl group and the fluorene ring.



(**9**) R=Me
(**10**) R=Et
(**11**) R=^{i}Pr
(**12**) R=^{t}Bu

^{13}*C NMR Spectra.* Above discussion implies that the deformation of molecular structure may exsist in

Table 2. ^{13}C NMR data of rotameric 9-arylfluorenes in $CDCl_3$ at room temperature (δ from TMS)

R	δ of 9-C		$^1J_{^{13}C-^1H}$ of 9-C	
	sp	ap	sp	ap
H[a]	53.93	53.93	128.8	128.8
Me	49.79	55.96	127.7	125.1
Et	49.26	56.28	126.7	124.8
^{i}Pr	48.90	56.33	127.6	122.7
^{t}Bu	50.97	59.66	127.2	115.4

a) The compound carries a methyl group in *p*-position.

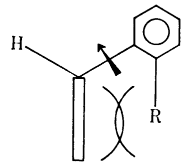


Fig. 2. Molecular deformation of the sp form.

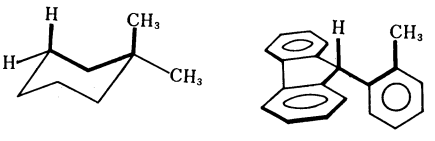
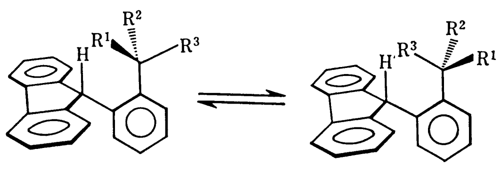


Fig. 3. The spacial arrangement of groups in 1,1-dimethylcyclohexane and **4**.



(A) **(B)**

Fig. 4. Conformation of the *o*-alkyl group in 9-arylfluorenes.

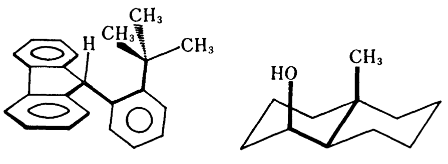
the ap form of compound **7**, since it is less stable than the sp form by at least *ca.* 2.5 kcal/mol. Several deformations are expected for the relief of the strain which is originated by the repulsion between the bulky *t*-butyl and the fluorene ring. Of those, bending of the C_9–C_{ar} bond outwards from the fluorene ring will be of most importance (Fig. 2). If such a deformation really exists, it will affect the chemical shift and the coupling constant (^{13}C–^1H) of 9-C, making them quite different from those of other normal 9-arylfluorenes. In Table 2 ^{13}C and ^1H NMR spectral data of rotameric 9-arylfluorenes are listed. In each case, 9-C gave two distinct signals corresponding to the sp and ap form. As for the chemical shifts of the ap forms, they tend to increase as the size of the alkyl group increases: this tendency is in accordance with the above assumption of molecular deformation, because bending of the C_9–C_{ar} bond outwards from the fluorene ring is expected to change the hybridization of 9-C sp²-like to cause the low field shift of the signal due to 9-C of the ap form. The degree of the low-field shift of the 9-C signals of the ap forms parallels somewhat with the increase in free energy difference between rotamers as the size of the alkyl group increases. In methyl, ethyl, and isopropyl derivatives the chemical shifts of 9-C lie within a small range of 0.4 ppm. Correspondingly free energy differences between rotamers are 0.3, 0.6, and 0.4 kcal/mol for the methyl, the ethyl, and the isopropyl compound. In the *t*-butyl derivative, however, the low field shift by about 3.3 ppm and the large free energy difference of more than 2.5 kcal/mol are observed. The correlation may be an indication that the population of 9-(2-alkylphenyl)fluorene is mainly regulated by the nonbonded interaction between the alkyl group and the fluorene ring. It may mean in turn that repulsion between the alkyl group and 9-H is relatively small.

Another method to check the presence of the molecular deformation, shown in Fig. 2, is the measurement of the ^{13}C–^1H coupling constant of 9-C. Inspection of Table 2 reveals that the coupling constants of the ap forms decrease as the size of the alkyl group increases. Since the magnitude of the ^{13}C–^1H coupling constant is correlated to s-character of the C-H bonding orbital, the decrease can be taken as an indication of the increase in p-character of the C–H bonding orbital.[8] This may most reasonably be caused by bending of the C_9–C_{ar} bond as shown in Fig. 2, though it may also be caused by widening any of the C–C–C angles at 9-C. As was seen in the chemical shifts of this series, the coupling constant of **7** showed a striking difference from those of other compounds. The value of 115.4 Hz may be one of the smallest C–H coupling constants ever reported for neutral molecules.[8]

As for the chemical shifts of 9-C of the sp-forms, they showed rather a complicated tendency as the size of the substituents increases: a large high field shift (4.1 ppm) was observed when a methyl group was introduced in 2′ position, whereas the shift was affected to only a small extent (0.9 ppm or less) on change of the methyl group by an ethyl or an isopropyl group. In contrast, a low field shift of *ca.* 2 ppm was observed when the alkyl changed from isopropyl to *t*-butyl. A large high field shift observed in the methyl compound may be attributed to the well-known γ effect, because the spacial arrangement of the 2′-methyl and 9-C in **4** is quite similar to that of an axial-methyl and 3-C in 1,1-dimethylcyclohexane (Fig. 3).[9] In both compounds the high field shift caused by the introduction of a methyl group amounted to *ca.* 4 ppm.

The most difficult point to explain is why the chemical shift of 9-C of compound **7** showed a relatively large low field shift. We tentatively consider that the difference in the prefered conformation of the alkyl group plays some role in determining the chemical shift of the sp form. Two stable conformations are possible for the alkyl group in position 2′. One is a conformation where 9-H squeezes in R¹ and R² (Conformer **A**) and the other is the one where 3′-H is situated between R¹ and R² (Conformer **B**) as shown in Fig. 4. In each conformation R³ opposes either 3′-H or 9-H. Thus the stability of two conformations must be decided by the relative bulkiness of R¹, R², and R³. In compound **6** where R¹ and R² are methyl and R³ is hydrogen, conformer **B** must be more stable than conformer **A**, because two methyl groups are placed within a repulsive region of 9-H in the latter, whereas the repulsive force between two hydrogens in the conformation **B** will be less. There is another possibility in conformation **A**: that is, the conformation where R^1 and R^3 are methyls and R^2 is hydrogen. Contribution of this conformation will be minor because the opposing effect of R^3 (CH_3) with 3′-H is large. Likewise, conformation **B** where R^1 and R^3 are methyls and R^2 is a hydrogen may contribute to only a small extent becuase of the opposing effect between R^3 and 9-H. Similarly the stable conformation of **5** is expected to be the one where an α hydrogen of the substituent is in proximity of 9-H. In this sense ethyl and isopropyl groups give similar steric effects on carbon at position 9 and thus the chemical shift of 9-C is almost invariable for the methyl, the ethyl, and the isopropyl compounds. In the case of compound **7**, R^1, R^2, and R^3 are all methyl groups and therefore **A** must be more stable than **B**: in **B** the distance between the methyl (R^3) and 9-H is quite small and a large repulsion is expected.

Then the spacial relation between 9-C and methyl carbon of this compound is quite similar to that between the methyl and the hydroxyl group of 4a-methyl-*trans*-1-decalol (**13**) (Fig. 5).[10] In **13** a downfield shift of *ca.* 3.4 ppm was observed and was attributed to the syn-axial arrangement of two interacting groups separated by four bonds. Thus the observed downfield shift of *ca.* 2 ppm may become a support for the δ effect originally described by Stothers *et al.*



(**7**) (**13**)

Fig. 5. The spacial arrangement of groups in **7** and **13**.

References

1) The preceding paper: M. Nakamura and M. Ōki, *Chem. Lett.*, 651 (1976)

2) Presented in part as a preliminarly form: M. Nakamura, N. Nakamura and M. Ōki, *Chem. Lett.*, **1977**, 17.

3) Present address: Department of Chemistry, School of Medicine, Toho University, Omorinishi, Otaku, Tokyo 143.

4) M. Ōki, *Angew. Chem. Int. Ed. Engl.*, **15**, 87 (1976).

5) T. H. Siddall, and W. E. Stewart, *J. Org. Chem.*, **34**, 233 (1969).

6) M. Nakamura, N. Nakamura, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **50**, 1097 (1977).

7) E. Dahlberg, B. Nilsson, K. Olsson, and P. Martinson, *Acta Chem. Scand.*, **B29**, 300 (1975).

8) Although the correlation between the s-character and the C–H coupling constant is questionable in highly straingd molecules (see, for example, L. S. Bartell and H. B. Bürgi, *J. Am. Chem. Soc.*, **94**, 5239 (1972)), the correlation holds to many compounds: J. H. Goldstein, V. S. Watts, and L. S. Rattet, *Prog. Nucl. Magn. Resonance Spectrosc.*, **8**, 103 (1971); T. L. Marshall, D. E. Miller, S. A. Conn, A. Seiwell, and A. M. Ihrig, *Acc. Chem. Res.*, **7**, 333 (1974).

9) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6612 (1967).

10) S. H. Grover and J. B. Stothers, *Can. J. Chem.*, **52**, 870 (1974).