^{19}F and ^{1}H Nuclear Magnetic Resonances of Chlorotrifluoroethylene–Isobutylene Copolymers

Kenkichi Ishigure,* Hirotada Ohashi, Yoneho Tabata, and Keichi Oshima

Department of Nuclear Engineering, University of Tokyo, Tokyo, Japan.

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ABSTRACT: ^{19}F NMR spectra of deuterated and nondeuterated samples of chlorotrifluoroethylene–isobutylene copolymers were measured and were found to be markedly dependent on temperature. The CF_2 resonances of the alternating copolymer were observed as two AB type quartets at lower temperature and the CFCl resonances were found to be a doublet of doublets, which apparently reverts to a triplet at higher temperature. From this result it was concluded, contrary to the suggestion previously made, that the copolymer is not stereoregular but has a random configuration. The CH_2 resonances of the ^{1}H spectra of the copolymers were successfully interpreted as two AB parts of ABX spectra. Discussion is also presented regarding the conformational structure of the copolymer on the basis of NMR data.

It has been shown in several papers[1–5] by the authors that fluorine nuclear magnetic resonance is a powerful tool to elucidate the structure of fluorine-containing copolymers. In the case of chlorotrifluoroethylene–isobutylene copolymers, CF_2 and CFCl resonances gave definite information about the sequence distribution of the copolymer as reported previously, but some uncertainty remains as to the configuration of the copolymer.[1,2] The CH_3 resonances of the copolymers were successfully interpreted in terms of triads and the assignment was consistent with the conclusion derived from the fluorine spectra. However, the CH_2 resonances were too complicated to give a consistent explanation. In the present paper ^{19}F NMR spectra were measured, at lower temperature than before, of alternating copolymers having higher solubility, probably because of lower molecular weight, and also of a copolymer of chlorotrifluoroethylene with isobutylene-d_8. This revealed a new aspect of the spectra and provided unambiguous information regarding the configuration and, in part, the conformation of the copolymers.

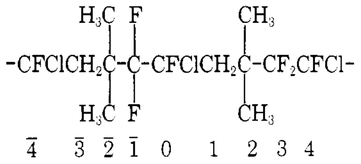
Experimental Section

Chlorotrifluoroethylene was prepared from 1,1,2-trichlorotrifluoroethylene by dechlorination with zinc dust in ethanol. Isobutylene-d_8 was prepared by dehydration of *tert*-butyl-d_{10} alcohol at 400 °C over alumina catalyst. Alumina catalyst was prepared by the dehydration and subsequent activation of aluminum hydroxide gel which was obtained by the neutralization of aqueous aluminum sulfate solution with sodium hydroxide. All the copolymer samples were prepared by γ-ray-initiated copolymerizations of both monomers. ^{19}F and ^{1}H NMR spectra were measured with a JEOL Model PS100 spectrometer operated at 94 and 100 MHz, respectively, in the temperature range of 60 to 120 °C. Benzotrifluoride was used as internal reference standard for fluorine resonance, and chemical shifts on the Φ^* (ppm) scale were evaluated by the addition of 63.7 (Φ value of benzotrifluoride) to the chemical shifts relative to benzotrifluoride.

Results and Discussion

(1) Fluorine Spectra. In Figure 1 the ^{19}F NMR spectrum (A) of an alternating copolymer measured at 60 °C is compared with that (B) measured at 100 °C. In previous work,[1] the alternating copolymer samples employed for the NMR measurement were prepared at 0 °C; samples obtained at 0 °C or higher temperature have rather low solubility, probably because of high molecular weight and high crystallinity. Consequently, it was quite difficult to obtain good resolution when the spectra were measured at temperatures below 100 °C. In the present work, the copolymerizations were carried out at lower temperatures, and the copolymer samples obtained were found to give well-resolved ^{19}F spectra even at lower temperature.

It is surprising that a marked temperature dependence is observed in the ^{19}F NMR spectra of the copolymer. The triplet at higher magnetic field in Figure 1B and the corresponding quartet in Figure 1A are assigned to CFCl groups, and the rest are attributed to CF_2 groups in the alternating sequence shown below, as in the previous paper.[1]



$$-CFClCH_2\underset{H_3C}{\overset{H_3C}{C}}-\underset{F}{\overset{F}{C}}-CFClCH_2\underset{CH_3}{\overset{CH_3}{C}}-CF_2CFCl- \qquad (1)$$

$$\bar{4}\quad \bar{3}\ \bar{2}\ \bar{1}\ \ 0\quad 1\ \ 2\ \ 3\ \ 4$$

The CF_2 resonance appears as an AB type quartet in Figure 1B, but when measured at temperatures below 70 °C, the higher magnetic field half of the CF_2 resonance is apparently composed of two components. This splitting is not considered to be due to vicinal F–F couplings because the consistent change is not seen in the CFCl resonance. Thus, the splitting is attributed to the chemical shift difference.

The geminal fluorine nuclei at carbon $\bar{1}$ in formula 1 are nonequivalent under the influence of the asymmetric centers, CFCl groups, in the chain. If the CFCl group of carbon $\bar{4}$ as well as that of carbon 0 has any appreciable effect on the chemical shift difference of geminal fluorine nuclei, then the CF_2 resonance is expected to split into two components corresponding to meso and racemic structures. This seems to be a quite reasonable and consistent interpretation of the experimental results which the authors failed to consider in the previous paper.[1] It should be noted that the words "meso" and "racemic" are used for convenience here, and that the racemic nuclei are not equivalent in this type of copolymer, unlike the usual vinyl-type polymers. It seems fortuitous that only the high-field half of the AB quartet shows the expected splitting, but it is interesting that a similar situation was found with the ^{19}F spectrum of the alternating tetrafluoroethylene–propylene copolymer.[4]

In Figure 2 is shown the ^{19}F NMR spectrum of an alternating copolymer of chlorotrifluoroethylene with isobutylene-d_8 measured at 100 °C. The CF_2 resonance is not subject to appreciable change by the deuteration of the copolymer, as expected from the structure of the copolymer, while the CFCl resonance appears as a doublet, the separation of which increases with decreasing temperature. The high-field half of the CF_2 resonance shows rather poorly resolved splitting at higher temperature, as in the case of nondeuterated copolymer.

Now it is evident that the apparent triplet at 116.7Φ^* in Figure 1B should not be considered to be a triplet, but to be two partly overlapping doublets, which separate to a

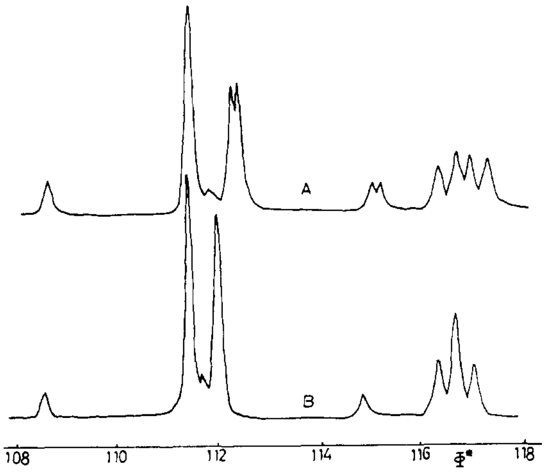
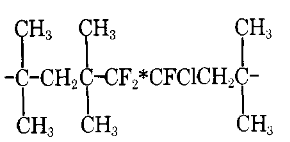


Figure 1. (A) ^{19}F NMR spectrum (94 MHz) of alternating copolymer measured at 60 °C in perchloroethylene. The copolymer sample was prepared at −78 °C and extracted with acetone for the elimination of polyisobutylene. (B) ^{19}F NMR spectrum (94 MHz) measured at 100 °C.

quartet at lower temperature. If the triplet at 116.7Φ* in Figure 1B is explained as the X part of an ABX type spectrum as reported previously,[1] this is expected to become a singlet upon deuteration of the copolymer, since the vicinal F–D coupling is negligibly small.

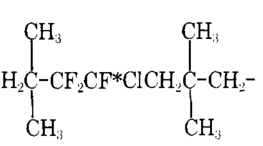
The splitting of the CFCl resonance in Figure 2 was not anticipated and seems rather confusing. As the copolymer sample employed for the measurement has a highly alternating structure, the splitting is considered to arise from the difference in the configurational structure of the copolymer. The central CFCl group in formula 1 has two asymmetric centers at the positions of carbon numbers 4 and $\bar{4}$. If these two asymmetric centers have a significant effect on the chemical shift of the central CFCl resonance, then the CFCl resonance has the possibility of splitting into four components corresponding to *mm*, *mr*, *rm*, and *rr*, where *m* and *r* refer to meso and racemic configuration, respectively. If the copolymer has a random configuration, the four components mentioned above are supposed to have equal intensity. Thus, it is inferred that two of the four components are overlapping with the rest in Figure 2.

It is interesting to compare the spectrum in Figure 1A with that of the isobutylene-rich copolymer shown in Figure 3. The quartet at the lower magnetic field was assigned to the CF_2 group of IIF*I sequence, and the doublet at 115.6Φ* was correspondingly attributed to IF*II, where F and I stand for chlorotrifluoroethylene and isobutylene monomer units, respectively.[2]



$$-\underset{CH_3}{\overset{CH_3}{C}}-CH_2\underset{CH_3}{\overset{CH_3}{C}}-CF_2{}^*CFClCH_2\underset{CH_3}{\overset{CH_3}{C}}-$$

IIF*I



$$-CH_2\underset{CH_3}{\overset{CH_3}{C}}-CF_2CF{}^*ClCH_2\underset{CH_3}{\overset{CH_3}{C}}-CH_2-$$

IF*II

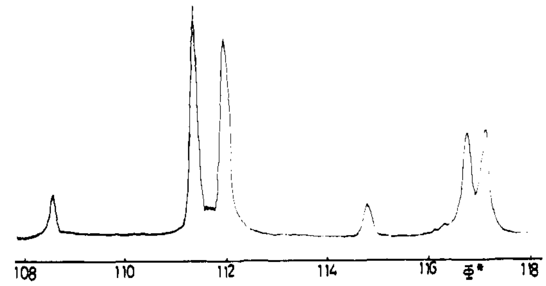


Figure 2. ^{19}F NMR spectrum (94 MHz) of alternating deuterated copolymer at 100 °C; solvent, perchloroethylene. The sample was prepared at −35 °C.

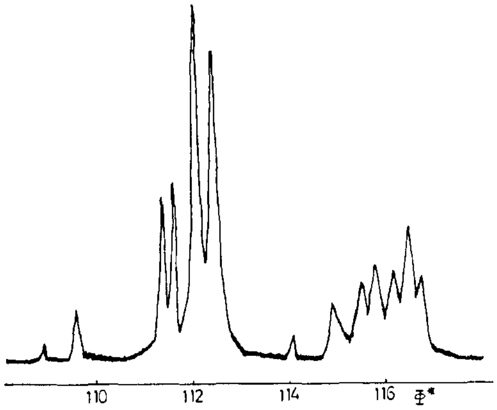


Figure 3. ^{19}F NMR spectrum (94 MHz) of isobutylene-rich copolymer (CTFE ca. 43 mol %) at 100 °C: solvent, perchloroethylene.

On assigning the above resonances, it was implied that the substituents at the six carbons on both sides have an observable effect on the chemical shift of the central fluorine resonance, but that the substituents at the fourth neighboring carbons have no effect on it. If the assignment is made within the scope of this criterion, there is no reason for the splitting of the CFCl resonance in Figure 2, because the central CFCl group has no asymmetric center at the six neighboring carbons ($\bar{3}$, $\bar{2}$, $\bar{1}$, 1, 2, and 3) on both sides in formula 1. Therefore, it is evident that the CFCl resonance is not interpreted in terms of tetrads, but pentads are taken into consideration in the following discussion. As far as the CF_2 resonance is concerned, no reason was found to have to take pentads into consideration.

Considering pentads, the doublet at 115.6 Φ* in Figure 3 should be attributed mainly to FIF*II and to IIF*II, if any. Though the upfield triplet, which is found to comprise two overlapping doublets, is identical with that appearing in the spectrum of the alternating copolymer, it is assigned to IIF*IF and FIF*IF, and that two components forming the triplet are considered to arise from the difference in the configuration of the copolymer and not from the difference in the monomer sequence. It follows that IIF*IF and IIF*II completely superimpose on FIF*IF and FIF*II, respectively, and that the substituents at $\bar{4}$ carbon in formula 1 have a much smaller effect on the chemical shift of the central CFCl group. Thus, the two doublets composing the triplet assigned to FIF*IF are assigned to (*mm*, *rm*) and (*mr*, *rr*), where two components in the parentheses are actually superimposed on each other and not observed as separate resonances.

Another possibility of assigning FIF*II and IIF*IF to the doublet at 115.6Φ* does not seem reasonable to the authors. The CFCl resonances attributed to FIF*II and IIF*IF are considered to be doublets since the vicinal H–F couplings will be similar in these sequences to those in FIF*IF. Therefore, if this alternative assignment is taken, FIF*II is expected to superimpose completely on IIF*IF. This, however, would be too fortuitous, because the substituents at three carbons ($\bar{4}$, 3, and 4) are different between FIF*II and IIF*IF sequences when the substituents at the eight carbons on both sides are taken into account.

It would be apparent from the above discussion that if it is assumed that the substituents at carbon 4 affect the CFCl resonance at carbon 0 but that those at carbon $\bar{4}$ do

Table I
Temperature Dependence of the Relative Intensities of CFCl Resonance

Polym temp, °C	I_{CFCl-l}[a]	I_{CFCl-h}[a]
−78	0.49	0.51
−35	0.52	0.48
0	0.50	0.50

[a] I_{CFCl-l} and I_{CFCl-h} are the relative intensities of lower field and higher field doublets of CFCl resonance, respectively.

Table II
Temperature Dependence of Spectral Parameters Measured from CFCl Resonance

Temp, °C	$\delta\nu_{CFCl}$, Hz	$(J_{AX} + J_{BX})_l$, Hz	$(J_{AX} + J_{BX})_h$, Hz
30	72	36	34
60	57	34	33
100	33	33	32
120	30	30	29

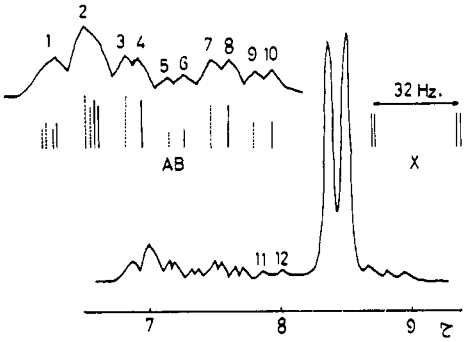


Figure 4. ^{1}H NMR spectrum (100 MHz) of alternating copolymer at 100 °C: solvent, perchloroethylene. The sample was prepared at 0 °C. The expanded CH_2 resonances are compared with calculated stick spectrum. Calculated spectrum of the CFCl resonance is also shown. A set of solid lines is an AB part of an ABX spectrum, ABX-I (Table IV), and the dotted lines are corresponding to ABX-II.

not, then the CFCl resonances of the alternating and nonalternating copolymers are interpreted quite consistently.

As shown in Table I, the relative intensities of the CFCl doublets assigned to FIF*IF are approximately equal to each other irrespective of polymerization temperature. Therefore, it is concluded, contrary to the suggestion in the previous paper,[1] that the copolymer assumes a completely random configuration in this temperature range of polymerization. In the case of chlorotrifluoroethylene–propylene copolymers, it was reported by the authors[5] that the configuration is not completely random when the copolymer is prepared at lower temperature and it approaches a random one as the polymerization temperature increases. This difference is inferred to arise from the fact that in the latter case the steric interactions take place between CFCl and $CH(CH_3)$ groups of the terminal radical and adding monomer in the course of copolymerization, while in the present system the interactions which mainly affect the steric configuration of the copolymer occur between two CFCl groups, one in adding monomer and another in the monomer neighboring to the terminal isobutylene, and are quite weak compared with those in the chlorotrifluoroethylene–propylene copolymer system.

In Table II is shown the temperature dependence of the chemical shift difference between two CFCl doublets assigned to FIF*IF, together with the separation of the components of each doublet. The chemical shift difference is seen to depend markedly on temperature as usual with fluorine resonances, but it is to be noted that the vicinal F–H coupling constants are also slightly dependent on temperature.

When the spectrum in Figure 2 is compared closely with that in Figure 1B, it is noted that the CFCl resonance appears at a little higher magnetic field in Figure 2. The chemical shift of a fluorine resonance is usually quite variable and sensitive to the conditions of the NMR measurement, especially to temperature and solvent. However, the difference between these spectra is apparently beyond the scope of the usual scattering of chemical shifts, and probably arises frim isotope shifts due to the neighboring deuterium substituents.

A weak peak at approximately 111.7Φ* appears to increase in intensity when the sample is polymerized at lower temperature; we cannot at present clearly explain it. It seems to be related to some irregular structure of the copolymers, probably to the terminal groups.

(2) Proton Spectra. It is essential to analyze the CH_2 resonance of the proton NMR spectra in order to explain the CFCl resonance completely. The CH_2 resonance, ranging from 6.5 to 8.1 τ, is quite complicated, as shown in Figure 4. If the CH_2 resonance is expressed as the AB part of an ABX type spectrum, it should be composed of, at most, eight lines. However, at least 12 peaks, numbered in Figure 4, are observed in the CH_2 region of the spectrum. Therefore, the CH_2 resonance is inferred to be composed of the AB parts of two ABX spectra. This seems quite reasonable, because the CH_2 group, having two asymmetric centers at the nearest and the third nearest carbons, as seen in formula 1, has the possibility of splitting into two components, corresponding to *m* and *r*.

As resonances 11 and 12 increase in relative intensities in the spectra of isobutylene-rich copolymers, they are evidently related to the isobutylene-rich sequences such as FII or IIF, which correspond to weak CH_3 resonances at 8.6 to 9.0 τ. The sum of the relative intensities of peaks 1 and 2 was found to be approximately equal to the sum of the intensities of peaks 3 to 10. Therefore, peaks 1 and 2 are two halves of the two AB parts of the ABX type resonances, comprising eight unresolved lines. The following relations among the line spacings were made use of for the assignment:

$$10 - 8 = 6 - 4$$
$$9 - 7 = 5 - 3$$

The calculations were repeated on the basis of an ABX spectrum until the best fit was obtained for the line spacings and intensities. The calculated spectrum is shown in Figure 4 as a stick spectrum, where a set of solid lines is the AB part of an ABX spectrum, ABX-I, and the dotted lines correspond to ABX-II. The calculated X part is also indicated in Figure 4, and the measured spacings of the doublets assigned to CFCl are approximately 33 and 32 Hz at 100 °C (Table II), being in good agreement with the calculated value of 32 Hz. The parameters used for the calculation are listed in Table III and the line spacings and intensities calculated using the parameters are represented in Table IV. In deriving the spectral parameters shown in Table III, the signs of the vicinal F–H and the geminal H–H coupling constants were assumed to be positive and negative,[6] respectively.

It is seen in Table III that the spectra ABX-I and ABX-II are different only in the chemical shift difference, $\nu_A - \nu_B$, and have the same coupling constants within experi-

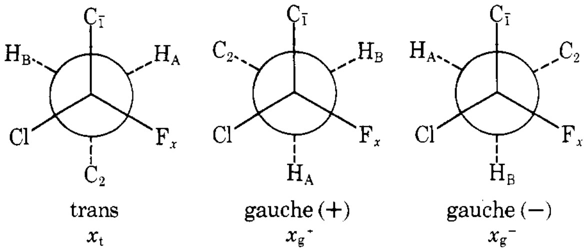
Table III
Spectral Parameters with Approximate Precision (Hz) Estimated from Comparison of Calculated and Measured CH$_2$ Resonances

	ABX-I	ABX-II
$\nu_A - \nu_B$	47.6 ± 2	42.2 ± 2
J_{AX}	0.5 ± 1	0.3 ± 1
J_{BX}	33.5 ± 1	33.7 ± 1
J_{AB}	−16.0 ± 1	−16.0 ± 1

mental error. It is of great interest to examine closely the values of the vicinal F–H coupling constants in Table III. One of the coupling constants, J_{BX}, is quite large (34 Hz), almost the upper limit of the vicinal F–H constants ever observed, while the other, F_{AX}, is approximately zero. There has been some controversy in regard to the relation between vicinal F–H constants and the dihedral angle, but it seems reasonable[7–9] to assume that $J_{HF(vic)}$ depends on the dihedral angle between the coupled nuclei in a way quite similar to the relationship between $J_{HH(vic)}$ and the corresponding dihedral angle, which was theoretically predicted by Karplus. According to this relationship, the coupling constant between *trans* H and F nuclei, J_t^{HF}, is much larger than J_g^{HF}, the coupling constant in the gauche conformation. The former is reported to range from 15 to 30 Hz in fluorinated ethane derivatives, while the latter is in the range of 1 to 5 Hz.

Internal rotations about the relevant C–C bonds of the present copolymers are considered not to be frozen out in the temperature range of the NMR measurements in the present work. Accordingly, if nuclei A, B, and X are defined as in formula 3 the coupling constants measured can be expressed as follows:

$$\begin{aligned}\langle J_{AX}\rangle &= x_t J_g^{HF} + x_{g^+} J_g^{HF} + x_{g^-} J_t^{HF}\\ \langle J_{BX}\rangle &= x_t J_t^{HF} + x_{g^+} J_g^{HF} + x_{g^-} J_g^{HF}\end{aligned} \qquad (2)$$



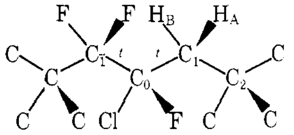
(3)

where x_{g^+}, x_{g^-}, and x_t refer to the mole fractions of gauche (+), gauche (−), and trans conformers with respect to the C$_0$–C$_1$ bond, and J_g^{HF} and J_t^{HF} are the vicinal H–F coupling constants between the nuclei at the positions of gauche and trans to each other, respectively. As mentioned above, normally, J_g = 1–5 Hz and $J_t \simeq$ 15–30 Hz. Thus, the values of J_{AX} and J_{BX} in Table III suggest that one of the geminal protons may be predominantly trans to vicinal F nucleus, while the other is mainly gauche. This leads to the possibility of predominance of trans and/or gauche (−) conformations with respect to the C$_0$–C$_1$ bond. In other words, x_t and/or x_{g^-} may be much larger than the other in eq 2. As the energy barrier for internal rotation is well known to be larger in fluorinated ethanes, it would not be unreasonable that trans and/or gauche (−) conformers are much more populated than the other in this copolymer. However, from qualitative stereochemical considerations, it appears that the trans conformation should be preferred over the gauche (−) conformation. Since the van der Waals' radius of chlorine atom is smaller than that of a methyl group, the steric repulsion force will be larger between two methyl groups than between a methyl group and a chlorine substituent, if the separations of two substituents are equal. Consequently, two gauche conformations with respect to the C$_0$–C$_1$ bond are less stable than the trans conformation in the present copolymer, because in the former the repulsion between two methyl groups or between a methyl group and the C$_3$ carbon is involved, irrespective of the conformation of the C$_1$–C$_2$ bond. This repulsive interaction, called "pentane effect", is known to make the conformations involved quite unstable.[10]

Table IV
Calculated Line Spacings and Intensities of ABX Spectra

		ABX-I		ABX-II	
Line	Origin	Position[a]	Intensity	Position[a]	Intensity
1	B	−49.5	0.76	−47.0	0.74
2	B	−33.5	1.24	−31.0	1.26
3	B	−17.0	0.54	−14.5	0.47
4	B	−1.0	1.46	1.5	1.53
5	A	16.5	1.24	14.0	1.26
6	A	18.0	1.46	15.5	1.53
7	A	32.5	0.76	30.0	0.74
8	A	34.0	0.54	31.5	0.47
9	X	−17.0	1	−17.0	1
10	X	−15.5	0.99	−15.5	0.98
11	X	15.5	1	15.5	1
12	X	17.0	0.99	17.0	0.98
13	Comb	−50.5	0.01	−45.5	0.02
14	Comb	50.5	0.01	45.5	0.02

[a] Line positions are expressed in Hz, and $\frac{1}{2}(\nu_A + \nu_B)$ and ν_X are taken to be zero for convenience. It is, however, to be noted that the origins of two ABX systems are not necessarily equal, and they are about 4 Hz separate from each other in the stick spectra (Figure 4).



(4)

The situation is entirely the same with respect to the C$_{\bar{1}}$–C$_0$ bond. Hence, trans conformations may be predominant in regard to both the C$_{\bar{1}}$–C$_0$ and C$_0$–C$_1$ bonds as shown in formula 4. The experimental results seem to support this conclusion, at least in part.

As to the conformations about the C$_{\bar{2}}$–C$_{\bar{1}}$ and the C$_1$–C$_2$ bonds, it is rather difficult to deduce predominant conformations from the qualitative stereochemical consideration because of severe steric repulsions of the substituents.

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