Configurational Characteristics of Poly(oxy-1,1-dimethylethylene). II. Conformations around the Skeletal C–C Bond as Determined by the Vicinal ^{13}C-^{1}H Coupling Constant Studies

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ABSTRACT: The ^{13}C natural abundance undecoupled NMR measurements were carried out on poly(oxy-1,1-dimethylethylene) (PODME) and its model compound, 1,2-dimethoxy-2-methyl-propane (DMMP) in neat liquid as well as in solution over a wide range of temperature. The solvents used were cyclohexane-d_{12}, methylcyclohexane-d_{14}, o-dichlorobenzene, and dimethyl-sulfoxide-d_6. Because of the limited solubility of PODME in conventional organic solvents, the measurements for the polymer were undertaken only in o-dichlorobenzene at higher temperatures. The analysis of the undecoupled CH$_3$ signals yielded the vicinal ^{13}C–C–C–H coupling constant, corresponding to an average of contributions from the three rotational isomers defined around the skeletal C–C bond. The values of ^3J_T and ^3J_G, and the energy difference between the *trans* and *gauche* conformers ($E_\sigma = E_g - E_t$) were determined from the temperature dependence of the vicinal coupling constant by the least-squares type analysis of Gutowsky. A value of $E_\sigma = 0.5$ kcal mol^{-1} was obtained for DMMP irrespective of the solvents used. Nearly the same value was deduced from the analysis of PODME. These results agree well with those obtained from the analysis of the experimental values of the dipole moment of DMMP in nonpolar solvents as reported in paper I. The values of ^3J_T and ^3J_G were estimated to be 4.8 ± 0.4 and 2.0 ± 0.2 Hz, respectively.

KEY WORDS 1,2-Dimethoxy-2-methylpropane / Poly(oxy-1,1-dimethyl-ethylene) / ^{13}C NMR / Vicinal Coupling Constant / Conformational Energy / *gauche* Oxygen Effect /

In the preceding paper[1] (referred to as paper I), the conformational equilibria for 1,2-dimethoxy-2-methylpropane (DMMP) were studied by analysis of the dipole moment data obtained in various nonpolar solvents. The conformational energy parameter E_σ defined for the skeletal C–C bond was estimated to be *ca.* 0.5 kcal mol^{-1} (1 cal = 4.2 J), a value of the same order of magnitude being obtained from the semiempirical energy calculations.[1]

In this communication, we have primarily studied the conformation dependence of the vicinal nuclear spin-spin coupling constants $^3J_{13_{CH}}$ associated with the moiety
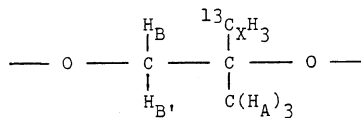
where the ^{13}C atom suffixed with X indicates the isotope existing in natural abundance. The coupling constant $^3J_{BX}$ may be defined as a rotational average such as

$$^3J_{BX} = (f_t/2)(J_T + J_G) + (f_g/4)(J_T + ^3J_G) \quad (1)$$

where the structural relations of J_T and J_G are shown in Figure 1. Fractions of the *trans* (f_t) and *gauche* conformers ($f_g = 1 - f_t$) around the central C–C bond can be estimated by using the statistical
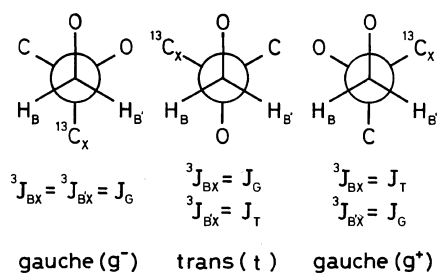
Figure 1. Three conformers of DMMP around the skeletal C–C bond, with definitions of the *trans* (^3J_T) and *gauche* couplings (^3J_G).

weight parameters introduced in paper I. For DMMP (*cf.* eq 3—5 of paper I),

$$f_t = 3/[3 + 2\sigma(2 + \omega' + 2\sigma'\omega + \sigma'\omega\omega')] \quad (2)$$

From an inspection of an appropriate model, we may obtain an expression for the internal residue of the poly(oxy-1,1-dimethylethylene) (PODME) chain (*cf.* eq 6—8 of paper I),

$$f_t = 3/[3 + 2\sigma(2 + \omega')] \quad (3)$$

The statistical weight parameters σ', ω, and ω' can be calculated for a given temperature from the results obtained in paper I. In keeping with the previous treatment,[1] σ is taken to be an unknown parameter. Thus, $^3J_{BX}$ is ultimately given as a function of ^3J_T, ^3J_G, and σ ($= \exp(-E_\sigma/RT)$). Following Gutowsky,[2] we shall determine ^3J_T, ^3J_G, and E_σ from the temperature dependence of $^3J_{BX}$. Since PODME is quite insoluble in conventional organic solvents at an ordinary temperature, the effect of solvents is investigated only for DMMP.

EXPERIMENTAL

Details of the DMMP sample are described in paper I. A high molecular weight sample of PODME[3] was generously supplied by Daicel Co. The solvents were all commercially available and used without further purification.

The ^{13}C natural abundance undecoupled NMR spectra were recorded on JEOL FX-60 and PS-100 NMR spectrometers equipped with FT and gated decouple systems. The former instrument was operated at a resonance frequency of 15 MHz over the temperature range 25—165°C. In the measurements, 3000 transients were accumulated with a 90°

rf pulse of 10 µs duration. The pulse repetition time was 5 s, which is five times as large as T_1 for the carbon nucleus of interest. NMR sample tubes with a diameter of 10 mm were used.

For the measurements at lower temperatures, the latter spectrometer (PS-100) was used. This instrument was operated at 25 MHz over the range -50 to 110°C. The number of transients accumulated for each 90° rf pulse of 20 µs duration was 800. The pulse repetition time was 10 s. An NMR sample tube with a diameter of 8 mm was used.

The temperatures were maintained within ± 1°C during the NMR measurements. Cncentrations of the sample solutions were *ca.* 20% (w/v).

RESULTS

Analysis of ^{13}C NMR Spectra

An example of the ^{13}C NMR spectra of PODME, obtained in *o*-dichlorobenzene by proton decoupl-

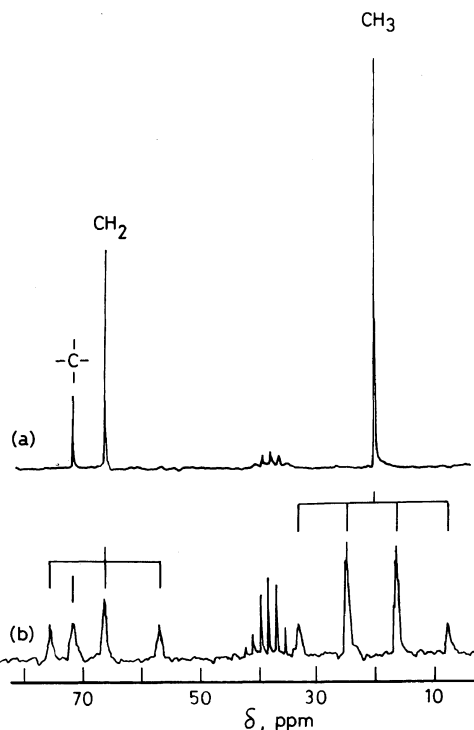**Figure 2.** The ^{13}C NMR spectra of PODME in *o*-dichlorobenzene at 155°C: (a) proton decoupling, 600 scans, and (b) gated decoupling, 1500 scans. Chemical shifts are expressed in ppm relative to tetramethylsilane. A septet found at about 40 ppm is due to dimethyl-sulfoxide-d_6 kept in a capillary for the ^{2}D lock.
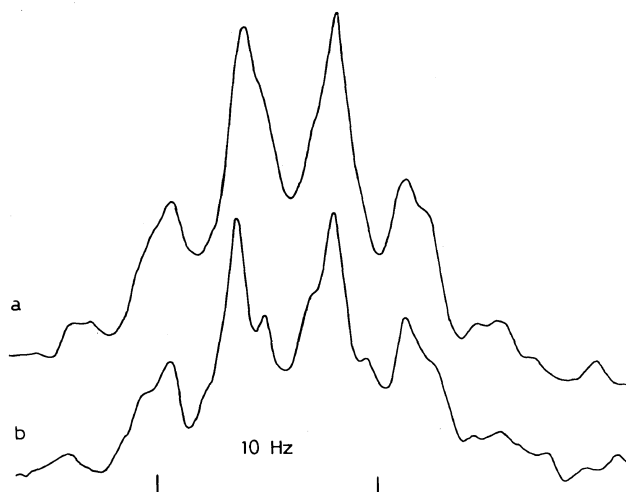
Figure 3. The ^{13}C NMR spectra of the pendant methyl carbon: (a) PODME in *o*-dichlorobenzene at 155°C, 3000 scans, and (b) DMMP in the same solvent at 70°C, 3000 scans.

ing, is shown in Figure 2a. Since the repeat unit of the polymer comprises three nonequivalent nuclei, the same number of sharp singlets were observed. When gated decoupling was applied, a proton coupled ^{13}C spectrum was obtained (Figure 2b). In this figure, a quartet located on the right arises from the articulated methyl carbons, a triplet in the center comes from the methylene carbon, and a singlet on the left is associated with the tertiary carbon carrying no directly-bonded protons. Further inspection of the spectrum reveals that each peak of the aforementioned quartet for the methyl carbons bears fine splittings due to vicinal couplings with protons. The corresponding spin system is $A_3BB'X$.

Shown in Figure 3 are the X spectra for DMMP and PODME. These two spectra are very much alike. The values of the effective BX vicinal coupling constant deduced from these figures should provide useful information regarding the conformation about the skeletal C–C bond. The vicinal ^{13}C–C–C–H coupling constants were therefore determined with the aid of the computer program LAOCN III,[4] and the results are summarized in Table I. All the spectra were resolved within a probable error ± 0.01 Hz. The observed vicinal coupling constants $^3J_{BX}$ decrease with increasing temperature in neat liquid as well as in solution. Methylcyclohexane-d_{14}, which has a freezing temperature lower than cyclohexane-d_{12}, was used in order to cover a wider temperature range.

Estimation of ^3J_T, ^3J_G, and E_σ from the Temperature Dependence of the Coupling Constant $^3J_{BX}$

As stated in the introductory part, the values of ^3J_T, ^3J_G, and conformational energy parameter E_σ can be determined from the temperature dependence of $^3J_{BX}$. Our method is essentially the same as that originally developed by Gutowsky.[2] The treatment is based on the assumption that variation in the population of rotational isomers is the major factor involved in causing such a temperature dependence of the vicinal coupling constant.[5] The conformational energy parameters E's are assumed to be effectively temperature independent.[6] Minimization of the sum of squares of nonlinear functions as given below was carried out according to the Powell method[7]:

$$f(x_1, x_2, x_3) = \sum_k [F_k^{\text{exptl}}$$

$$- F(x_1, x_2, x_3, E_\sigma, E_\omega, T_k)]^2 \quad (4)$$

where F_k^{exptl} indicates the experimental value observed at temperature T_k, and F the analytical expression as a function of x_1, x_2, x_3, and T_k. The subscript k specifies the number of experimental data. The variables x_1, x_2, and x_3 correspond to ^3J_T, ^3J_G, and E_σ, respectively. The parameters E_σ, E_ω, and E_ω, were taken from Table III of paper I. The minimum of f was searched by iteration starting from the best trial values of ^3J_T, ^3J_G, and E_σ.

The values of ^3J_T, ^3J_G, and E_σ determined in this

Table I. Temperature dependence of the vicinal coupling constants $^3J_{BX}$ for DMMP and PODME

DMMP in cyclohexane-d_{12}

T	$^3J_{BX}$
°C	Hz
25	3.21_0
40	3.20_4
55	3.20_1
70	3.18_6
80	3.18_4

DMMP in methylcyclohexane-d_{14}

T	$^3J_{BX}$
°C	Hz
−50	3.25_6
−10	3.24_2
0	3.23_7
26	3.23_1
35	3.22_7
45	3.22_4
56	3.20_2
68	3.19_1
74	3.18_0
84	3.17_8
88	3.17_5
108	3.16_6

DMMP in *o*-dichlorobenzene

T	$^3J_{BX}$
°C	Hz
25	2.94_9
40	2.93_2
50	2.92_0
70	2.91_9
100	2.90_8

DMMP in dimethylsulfoxide-d_6

T	$^3J_{BX}$
°C	Hz
25	2.96_4
45	2.95_2
60	2.94_4
80	2.93_8
100	2.92_4

DMMP (neat liquid)

T	$^3J_{BX}$
°C	Hz
26	3.28_9
42	3.28_7
57	3.25_2
70	3.24_9
90	3.24_2

PODME in *o*-dichlorobenzene

T	$^3J_{BX}$
°C	Hz
110	3.12_4
127	3.12_0
140	3.10_8
155	3.08_6
167	3.08_0

manner are listed in Table II. The analysis established unambiguous values for these parameters, except for the usual uncertainty in the absolute sign of the J's. The dielectric constants of the solvents used[8] are also included for reference.

DISCUSSION

As shown in Table II, the values of ^3J_G remain nearly constant (2.0 ± 0.2 Hz), irrespective of the solvents used. The corresponding values of ^3J_T are slightly more scattered within the range 4.8 ± 0.4 Hz. The results obtained for the polymer (PODME) in *o*-dichlorobenzene (110—167°C) were found to be nearly identical with those for the model compound (DMMP) deduced in the same solvent, but over a somewhat lower temperature range. Barfield[9] carried out theoretical calculations of vicinal ^{13}C-^{1}H coupling constants for a variety of molecular systems by using the semiempirical INDO-finite perturbation theory.[10] He obtained ^3J ($\phi = 0$) = 8.78 and ^3J ($\phi = 120$) = 1.97 Hz for pro-

Table II. The best-fit values of ^3J_T, ^3J_G, and E_σ of DMMP and PODME deduced from the analysis of the temperature dependence of $^3J_{BX}$

Compound	Solvent	Dielectric constant of solvent[a] (25°C)	^3J_T Hz	^3J_G Hz	E_σ kcal mol^{-1}
DMMP	Cyclohexane-d_{12}	2.02	5.0 ± 0.5	2.0 ± 0.2	0.50 ± 0.05
	Methylcyclohexane-d_{14}	2.02	5.1 ± 0.4	2.0 ± 0.1	0.50 ± 0.04
	Neat liquid		5.2 ± 0.5	2.0 ± 0.2	0.50 ± 0.05
	o-Dichlorobenzene	9.93	4.4 ± 0.5	2.0 ± 0.2	0.50 ± 0.06
	Dimethylsulfoxide-d_6	46.7	4.4 ± 0.5	2.0 ± 0.2	0.50 ± 0.06
PODME	o-Dichlorobenzene	9.93	4.9 ± 0.7	2.0 ± 0.2	0.50 ± 0.08

[a] Reference 8.

pane in the regularly staggered conformation: for the former coupling constant, a value of $^3J_T = 13 \pm 1$ Hz was estimated from the experiment.[11] A better agreement was found for the ^3J_T values of some cycloalkanes such as cyclohexane and adamantane.[12] It has been known that the magnitude of the vicinal coupling constant tends to decrease with substitution of electronegative groups at the β and γ positions. Forrest and Sukumar[13] concluded from studies on a series of t-butyl derivatives ($^{13}CH_3C(CH_3)_2Y$: $Y = D$, CH_3, I. Br, Cl, F) that the $^3J_{CH}$ value decreases with the electronegativity of substituent Y. A similar trend has been observed for ^1H-^1H vicinal coupling constants.[14] Barfield, Marshall, and Canada[12] examined the γ-effect on $^3J_{CH}$: the value of ^3J ($\phi = 0$) calculated for 3,3-dihydroxypropane ($^{13}CH_3CH_2CH(OH)_2$) was in the range 5.30—6.55 Hz. No examples were found in the literature for 2,3-disubstituted compounds with which our results may be directly compared.

The value of E_σ of DMMP was estimated to be ca. 0.5 kcal mol^{-1}, indicating that the trans form is more stable than the gauche form, in all the solvent systems employed. The solvents used in this study cover a range of dielectric constants from 2.02 to 46.7 (Table II). The observed insensitivity of E_σ to the polarity of the media throughout this range may be somewhat inconsistent with what one might expect from the results reported on some 1,2-dihaloethanes,[15] whose rotational equilibria have been known to be largely solvent dependent. The magnitude of the conformational energy E_σ obtained above agrees favorably with those (0.4—0.8 kcal mol^{-1}) deduced[1] from the analysis of the

dipole moment of DMMP in nonpolar solvents such as benzene, carbon tetrachloride, and cyclohexane. Because of the limited solubility of PODME in organic solvents, the value of the same energy could be estimated for the polymer only in o-dichlorobenzene at higher temperatures. The result was found to be identical with that of DMMP within experimental error.

The theoretical value of E_σ evaluated by using semiempirical potential energy expressions was 0.5 kcal mol^{-1} as described in paper I. The agreement between theory and experiment again suggests that the gauche oxygen effect[16] is entirely suppressed in DMMP as well as in PODME.

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