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C–C and C–O bond conformations in 1,2-dimethoxyethane, *bis*-(2-methoxyethyl)ether and poly(ethyleneoxide): dependence on solvent and temperature

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Data from $^3J_{HCCH}$ and $^3J_{HCOC}$ couplings in 1,2-dimethoxyethane and bis-(2-methoxyethyl)ether, plus $^3J_{HCCH}$ in poly(ethylene oxide), have been obtained in five solvents by iterative fitting. The resulting proportions of *gauche* rotamers are higher than previous estimates, and higher still after allowance is made for the pentane effect. They fit well with gas phase electron diffraction data, with current gas phase theoretical calculations and with standard RIS parameters for the polymer, but less well with calculations for the liquid state. The influence of solvent arises more from variations in its H-bond donor properties than in its dielectric. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

There has been considerable recent interest in determining the conformational preferences of 1,2-dimethoxyethane (DME)[1–3], both as a guide to the molecular modelling[4–11] of the widely used poly(ethylene oxide) (PEO) and also because the rotameric distribution about the C–O bond seems to have considerably more *gauche* contributions than expected from simple methods of modelling. This also has implications for the modelling of related molecules, such as crown ethers, and even of the glycosidic bond. The dependence of the rotameric distributions on solvent is also central to understanding the widespread industrial use of PEO and of block copolymers of PEO with, e.g. poly(propylene oxide) to create non-ionic micelles. We have therefore sought to amplify existing measurements on DME by extending the range of solvents in which it is studied, by a parallel study of the next highest oligomer, *bis*-(2-methoxyethyl)-ether (BMEE) and also by using samples of PEO itself, of relatively low molecular mass.

N.m.r. is highly suited to the quantitative investigation of these rotameric states. The ^{13}C sidebands in the ^{1}H n.m.r. spectra of DME and of PEO arise from an isotopomer in which the H degeneracy is partially removed, so that both of the $^3J_{HH}$ values may be deduced by subspectrum simulation. The same patterns occur in the main, ^{12}C isotopomer of BMEE. These coupling constants may be converted into rotamer proportions using a well-parameterized Karplus relationship[12,13]. Also, the fully coupled ^{13}C n.m.r. spectra of DME and of BMEE permit the computerized extraction of all the $^2J_{CH}$ and $^3J_{CH}$ coupling constants, including the C–O–C–H couplings which enable study of the C–O bond. For this case the Karplus parameters are somewhat less certain, but can nevertheless be established with acceptable accuracy as described below. The corresponding $^3J_{CH}$ data can be extracted for normal PEO in solvents where it has adequate solubility. Also, there are a few combinations of solvent and ether for which some polymer couplings, e.g. for endgroups, cannot be reliably interpreted because of inconvenient coincidences of multiplet components. However, these lacunae can be reasonably filled by extrapolation.

Some solvents also permit sufficient variation of temperature for the approximate extraction of ΔH as well as ΔG values. These imply that ΔS for the $g \leftrightarrow t$ transition can be significant.

EXPERIMENTAL

All n.m.r. spectra were recorded using a Bruker ACP400 spectrometer, and if second order, analysed iteratively using Bruker's WIN-DAISY program. The coupled ^{13}C spectra typically required overnight accumulation, even using gated ^{1}H pre-irradiation. The outer, and thereby

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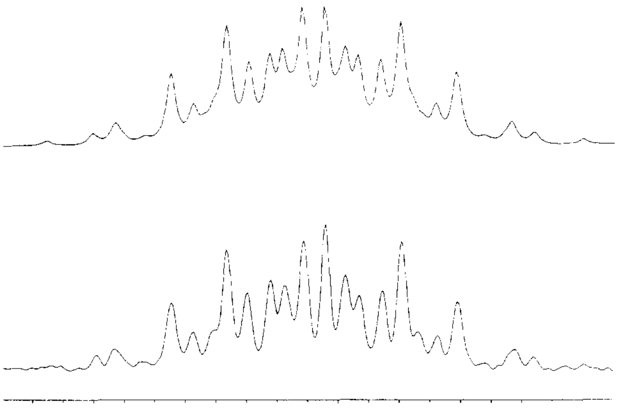

Figure 1 (Lower trace) Left-hand component of fully ^1H-coupled ^{13}C n.m.r. 'triplet' of PEO 6000 in dioxan-d_8, 353 K. (Upper trace) Iterated simulation of an inner ^{13}C-spin in the 9-spin tetramethylene system. Axis units are 1 Hz

simpler components of the main ^{13}C multiplets were selected for the analyses, which were based on an AA′BB′ spin system (^1H) and AA′BB′X (^{13}C). No $^4J_{CH}$ couplings were resolvable, and so they were not included in the simulations, although they are probably responsible for some line broadenings. A typical fit is shown in *Figure 1*. The estimated errors in ^3J are ±0.1 Hz.

DME was obtained from Sigma Chemicals and BMEE and PEO (M_n = 600 and 6000) from Aldrich; all were used without further purification. The concentrations for the variable solvent data were 2% w/w, with 5% w/w for the temperature variations.

RESULTS

Variation with solvent

Table 1 shows the ^3J couplings measured for the three ethers, in various solvents at 295 K. It also shows the total percentage of *gauche* rotamers for each bond, calculated via the Karplus relation. The HCCH couplings were assumed to follow the relationship used by Tasaki and Abe[1], with $^3J_{HH}(gauche) = 2.3$ Hz and $^3J_{HH}(trans) = 11.4$ Hz in all solvents. Thus we follow their approximation that one averages any slight variation of these coupling contributions, between and within the 3 rotamers of a given bond.

No such Karplus relationship has been established for $^3J_{CH}$ across methoxyl C–O bonds, except for HCOC couplings at the anomeric carbon in disaccharides, where $^3J_{CH}(trans) \sim 6.8$ Hz. Anderson[14] has deduced the relation $^3J_{COCH} = 7.6\cos^2\phi - 1.7\cos\phi + 1.6$ for methylcyclohexanes, but although the $\phi = 0°$ value used to derive this was well determined, the $\phi = 90°$ value was less fully parameterized. Alternatively, one may note that $^3J(trans)/^3J(gauche) = 5.0$ in many different Karplus relationships. Now the present measurements included that of $^3J_{COCH}$ for the methyl protons (J_{Me}), with observed values ranging from 4.9 to 5.2 ppm and varying slightly with both temperature and solvent. These must necessarily be the average of one *trans* plus two *gauche* couplings. Thus the *gauche* $^3J_{COCH}$ coupling must be $3J_{Me}/7$ and the *trans* must be $15J_{Me}/7$ for each solvent used. These observations lead to Karplus relationships very similar to that deduced by Anderson (e.g. $J_t = 11.0$, $J_g = 2.2$ in C_6D_{12}) but with slightly greater variation of J

Table 1 Variation of couplings and rotamer probabilities with solvent at 295 K

	C_6D_6		Dioxan-d_8		DMSO-d_6		$CDCl_3$		D_2O	
Bond	^3J (Hz)	% *g*	^3J (Hz)	% *g*	^3J (Hz)	% *g*	^3J (Hz)	% *g*	^3J (Hz)	% *g*
DME C–C[a]	6.10 3.78	*84*	6.10 3.92	*82 (80)*[e]	6.16 3.33	*87 (85)*[e]	6.27 2.88	*94*	6.42 2.45	*98*
DME C–O[b]	3.66	*34*	3.62	*33 (39)*	3.57	*31 (38)*	3.15	*23*	3.12	*25*
BMEE C–C[a]	6.10 3.82	*83*	6.14 3.87	*82 (80)*	6.21 3.38	*88 (83)*	6.25 3.26	*90*	6.40 2.60	*99*
BMEE, inner C–O[c]	3.35	*26*	3.36	*27 (32)*	3.11	*21 (30)*	3.11	*21*	2.71	*14*
BMEE, outer C–O[b]	3.60	*31*	3.51	*30 (37)*	3.48	*29.1 (36)*	3.12	*21*	2.99	*21*
PEO 600, central C–C[a]					6.10 3.47	*87*			6.62 2.59	*97*
PEO 600 endgroups, C–C[a]					6.03 4.54	*75*			6.32 2.97	*93*
PEO 6000, C–C[a]	6.04 3.97	*82*	6.15 3.99	*81 (80)*	6.28 3.37	*88 (81)*	6.07 3.68	*85*	6.23 2.55	*97*
PEO 6000 endgroups, C–C[a]	6.19 3.23	*90*	6.08 3.51	*87*						
PEO 6000, C–O[d]			(3.65)	*(34)*	(3.59)	*(32)*				
Isolated bond probabilities[d]										
C–C		*42*		*41 (41)*		*44 (43)*		*46*		*49*
C–O		*17*		*16 (20)*		*15 (19)*		*12*		*11*
α_1[f]		0		0		0		0.44		1.17
β_1[g]		0.10		0.37		0.76		0		0.18

[a] From $^3J_{HCCH}$
[b] From $^3J_{C(methyl)OCH}$
[c] From $^3J_{CO(central)CH}$
[d] % Probability of a single *gauche* rotamer, after RIS allowances, calculated from DME and BMEE data only (see text)
[e] Bracketed figures obtained at 353 K
[f] Taft solvent H-bond donor parameter
[g] Taft solvent H-bond acceptor parameter

Table 2 Variation of $t \leftarrow g$ equilibria with temperature

Ether	Solvent	Bond	ΔH^a (kJ mol)$^{-1}$	ΔS (J K^{-1} mol^{-1})	ΔS (statistical)^c
DME	Toluene-d_8	C–C	3.35	−2.41	−5.76
DME	Toluene-d_8	C–O	−3.94	−6.87	−5.76
DME	C_6D_{12}	C–C	2.04	−3.84	−5.76
DME	C_6D_{12}	C–O	−2.83^b	−4.78^b	−5.76
BMEE	DMSO-d_6	C–C	4.99	0.85	−5.76
BMEE	DMSO-d_6	C–O (inner)	−4.65	−6.52	−2.39
BMEE	DMSO-d_6	C–O (outer)	−4.63	−8.50	−5.76
BMEE	C_6D_{12}	C–C	2.49	−2.37	−5.76
BMEE	C_6D_{12}	C–O (inner)	^{b}	^{b}	−2.39
BMEE	C_6D_{12}	C–O (outer)	−2.49	−2.90	−5.76
PEO 6000	DMSO-d_6	C–C (main)	6.38	5.78	−5.76

[a] $K = t/g^{(+\text{ and }-)}$

[b] Not reliably determined

[c] From RIS calculation (see Results section) only retaining the pentane effect

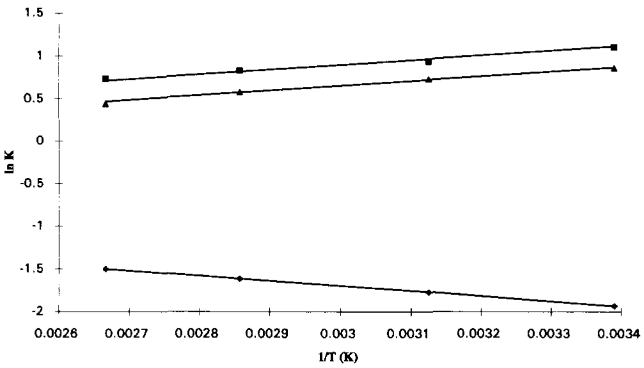

Figure 2 Temperature dependence of K $(= t/g^{(+\text{ and }-)})$ for three typical BMEE bonds in DMSO-d_6. Upper trace, central C–O bonds. Middle trace, terminal C–O bonds. Lower trace, C–C bonds

with ϕ, at both extremes, and a weak dependence on solvent. The proportions of *trans* and *gauche* rotamers can then be calculated from $^3J(observed)$ if one makes the usual simplifying assumption given above.

Variation with position

The final part of *Table 1* shows the *gauche* probabilities deduced for isolated C–C and C–O bonds, by considering the five experimental values, in each solvent, found for both DME and for BMEE, and then fitting these by an RIS calculation[15]. These isolated-bond probabilities respectively correspond to the standard RIS σ' and σ matrix elements. The calculation required a suitable assumption about the probability of any g^+g^- diad, i.e. about the size of the pentane effect, or equivalently of the RIS β or ω factor. This probability was taken here to be the same as deduced by Mark and Flory[15], i.e. zero for C–O–C but 0.8 for C–C–O; our data did not convincingly support attempts to find a different, fitted value. The calculation predicts, not surprisingly, that *gauche* rotamers occur more easily at the terminal C–O bonds than at the centre of the molecule. This is borne out by the data in *Table 1*, within experimental error. As an example, the experimental values for dioxane solvent, at 295 K, with the fitted values in brackets alongside, are 82 [82] and 33 [31] for DME and 82 [82], 30 [31] and 27 [27] for BMEE, where the last figures refer to rotations about the inner C–O bonds.

The relatively small variations of *gauche* proportions between DME and BMEE suggest that PEO will not differ greatly in its rotameric populations, from those of the inner groups of BMEE. This is borne out by the PEO 600 and PEO 6000 couplings, given for various solvents in *Table 1*. The same table also records HCCH couplings for the terminal $-OCH_2CH_2OH$ units (endgroups) of these polymers, where obtainable. Because of the shift inequivalence of the methylene pairs in this terminal unit, their couplings may be observed directly rather than *via* the ^{13}C sidebands. This renders them detectable in at least some solvents.

Variation with temperature

Table 2 shows ΔH and ΔS values for the $g \rightarrow t$ transition, deduced from the temperature variation of the five couplings in DME and BMEE, each in two solvents. The errors in these thermodynamic values may be substantial, because the variations of calculated population with temperature are quite sensitive to small and non-systematic errors in the measured couplings. Nevertheless, reasonable Van't Hoff plots are obtained, as exemplified in *Figure 2*. The values of ΔS are also compared with those calculated statistically from the fraction at $1/T = 0$, i.e. deduced by setting all rotamer probabilities equal except for those forbidden by the pentane effect between carbon atoms. K (i.e. t/total g) and hence ΔG led to ΔS (statistical) when ΔH (statistical) was set to zero. The experimental ΔS values are not highly reliable, but they differ significantly in some cases from the statistical value.

DISCUSSION

The rotamer populations in *Table 1* underline and extend earlier, corrected deductions from n.m.r. measurements, which were not based on direct, iterative fitting of the couplings[1]. They show the smaller $^3J_{HH}$ coupling to be even smaller than previously measured, especially in D_2O. This means that the C–C bond can be as much as 98% *gauche*. The simple rotational isomeric state (RIS) analysis, described above, emphasizes this further by estimating the *gauche* probability for an isolated bond, i.e. by disentangling this from the pentane effect in the complete molecule, which itself tends to favour *trans* rotamers. In its absence, the total *gauche* probability about the C–O bond rises to between 23% and 33% at 295 K, and of course higher at 353 K. The calculation is certainly naive in assuming that the rotamer populations are determined solely by the rotational properties of individual bonds, plus a pentane effect. Nevertheless, it does reproduce a general trend of the DME plus BMEE data, that the *gauche* probability increases at the outer C–O bonds.

The n.m.r. data, particularly in benzene and dioxane, fit well with electron diffraction data on DME[16]. These gas-phase data should compare closely with data in a non-polar solvent, such as benzene, and also with the dioxan data, because Inomata and Abe[2] have shown that the n.m.r. couplings for gaseous DME extrapolate almost linearly with temperature from those in the liquid phase. The diffraction data points to dominance of the *tgt* and *tgg* conformations with the C–C bond 79% *gauche* and the C–O bonds each 36% *gauche* on average, at 273 K. The corresponding n.m.r. values in dioxane at 295 K are 83% and 32%.

They also fit well with the σ and σ' RIS parameters deduced in Flory's classical papers[15,17] from the variation of stress, characteristic ratio and dipole moment of PEO with temperature. Mark and Flory also assumed the rigorous exclusion of g^+g^- and g^-g^+ conformations caused by rotations in a C–O–C portion of the polymer backbone, but they were able to deduce a less rigorous exclusion of the corresponding conformations in a C–C–O portion. Their suppression factors, (β or ω), for the latter ranged from 0.566 to 1. They give corresponding ranges for σ', the $g^{(+\text{ or }-)}/t$ probability for the C–C bond alone, to be 1.8–2.07, at 60°C in good solvents such as benzene. The equivalent figures from our 80°C data are 2.1 in dioxan and 2.8 in DMSO. For C–O rotations, i.e. for the σ factor, Mark and Flory quote 0.055–0.220 as an acceptable range of fits to 60°C data, with most of their calculations giving figures towards the higher end of this range. Our 80°C figures are 0.16 (dioxan) and 0.15 (DMSO). Thus our methylated monomer and dimer data strongly support Mark and Flory's earlier deduction of a substantial *gauche* rotameric population about both bond types, but predict it to be even larger in some solvents. These deductions are supported by our direct measurements on the non-terminal parts of PEO at 353 K in dioxan and DMSO, for these show very similar proportions of *gauche* rotamers to the average of those in BMEE. The extrapolation from oligomer to polymer is also supported in *Table 1* by the 295 K data on PEO 600.

The solution data also fit well with either *ab initio* or parameterised force field gas-phase calculations, for these predict around 79% of *gauche* C–C and 27% of *gauche* C–O rotamers at 273 K[9]. However, Smith *et al.* predict a rather lower probability of 20% for C–O *gauche* in the liquid state[4]. They attribute this drop to intermolecular competition for strong 1.5 CH . . . O electrostatic interactions. Our observations in, e.g. dioxane solution do not support this, although we do observe a comparably lower proportion of C–O *gauche* in H-bonding solvents.

The solvent influences listed in *Table 1* yield a regular countertrend, within experimental error. The proportion of *gauche* C–O bonds falls as that of *gauche* C–C bonds rises, even after allowance for the pentane effect. This may be because of the different local dipoles in the various subunit rotamers. For example, the *tgt* conformer might be favoured over *tgg* and *ttt*, perhaps because it best permits interaction with a solvent molecule. However, this countertrend may also be a subtle influence of long-range excluded volume effects, in a polymer with such a high proportion of *gauche* bonds. A second trend is that the proportion of *gauche* C–O bonds correlates with the Taft H-bond donor (α_1) and acceptor (β_1) properties of the solvent[18], with the donor properties having markedly the greater weighting. This explains why chloroform has such a strong influence. It is probably affecting the C–O bonds through the *gauche*-oxygen effect[19], by H-bonding to the oxygen lone pairs. The weaker, additional influence of the solvent acceptor properties is only apparent in the other three solvents. Their Taft β_1 parameters are in the order DMSO > dioxane > benzene, which is the reverse of the % C–O *gauche* order. This may reflect the proposal from Smith *et al.*, noted above, that an acceptor solvent disrupts internal H-bonding in the ether. Earlier work[1] proposed that the influence of solvent on PEO was mediated by the solvent dielectric. Our data, using a wider range of solvents, does not fully support this analysis, but instead shifts the emphasis towards H-bonding by the solvent.

The conformations of the endgroups listed in *Table 1* show that both water and DMSO reduce the probability of the terminal C–C bond being *gauche*, whereas benzene and dioxane increase it. The differences between the inner and the terminal groups must very largely arise from the –OH group on the latter. It is probable that this forms H-bonds to water or DMSO, and that these have the effect of extending the group out from the polymer into the solvent. Benzene and dioxane, on the other hand, may cause the chain end to turn inwards and H-bond to other parts of the polymer chain instead.

Contributions from ΔS are often ignored in comparisons between experiment and theory. The observations in *Table 2* may show that some of the remaining discrepancies arise because the non-statistical contributions to ΔS are not in fact negligible, especially in the case of the polymer.

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