

# An Investigation of the Molecular Structure and Conformation of Dipropyl Ether, $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—O—CH}_2\text{—CH}_2\text{—CH}_3$ , in the Gas Phase

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The molecular structure of dipropyl ether has been investigated in the gas phase by the electron diffraction method. Satisfactory agreement between experimental and theoretical data is obtained for an equilibrium mixture of 26(6) % *aaaa* and 74(6) % *g±aag±* conformers. However, also the *aaag* conformation alone gives an acceptable correspondence to the experimental data. Consequently, any proportion of a mixture of the *aaaa/g±aag±*, where the ratio 26:74 is maintained, and the *aaag* conformer will also be a solution to the problem. Despite this impossibility to obtain a unique solution it is concluded that strong attractive 1,4-CH...O interactions cannot be present. Independently of conformation the bond distances and valence angles are found to be the following:  $r(\text{O—C})=1.404(6)$  Å,  $r(\text{C—C})=1.524(8)$  Å,  $r(\text{C—H})=1.116(6)$  Å,  $\angle\text{COC}=116.1(3.6)^\circ$ ,  $\angle\text{OCC}=109.1(1.5)^\circ$ ,  $\angle\text{CCC}=113.5(1.8)^\circ$ ,  $\angle\text{CCH}(\text{methyl})=114.7^\circ$ ,  $\angle\text{HCH}(\text{methylene})=108.0^\circ$ .

Earlier investigations of ring systems like 1,5,9,13-tetraoxacyclohexadecane<sup>1,2</sup> and of polymer chains like poly(trimethyleneoxide)<sup>3</sup> in the crystalline state have shown that each  $-(\text{O—CH}_2\text{—CH}_2\text{—CH}_2)_n\text{—}$  unit prefers one unique conformation, where the dihedral angles  $\delta(\text{COCC})$  are *anti* and  $\delta(\text{OCCC})$  are *gauche*. From these observations it seems reasonable to assume that 1,4-CH...O interactions are present in molecules of this type.<sup>9</sup>

It was therefore of interest to investigate the molecular structure of simpler molecules in the gas phase by the electron diffraction method in order to see if the 1,4-CH...O *gauche* interaction is attractive also when no crystal forces are present. Among such model compounds 1,3-dimethoxypropane would be chemically

most similar, but also dipropyl ether would potentially have such interactions although the CH involved here is less acidic.

## EXPERIMENTAL

The sample of dipropyl ether used in the experiment was delivered from Fluka.

The electron diffraction experiment was performed on a Balzers Eldigraph KDG2. The scattering diagram has been recorded at two different nozzle-to-plate distances, *i.e.* 579.85 and 250.12 mm. The wavelengths of the electrons were 0.05851 and 0.05855 Å, respectively. The pressure measured in the apparatus during the exposure was about  $6 \times 10^{-6}$  Torr. The sample was kept at approximately 0°C. Four selected photographic plates recorded at each nozzle-to-plate distance were used in the structure analysis. The intensity of the scattering was recorded on a photometer for each

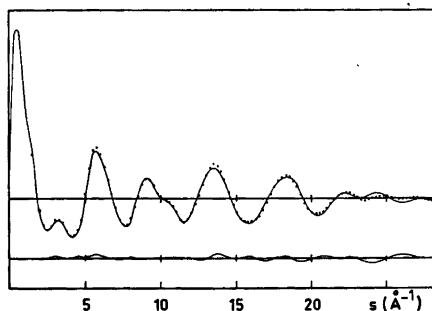


Fig. 1. Dipropyl ether. Theoretical molecular intensity curve. The dots show the experimental values. The lower curve shows the difference between the experimental and theoretical values.

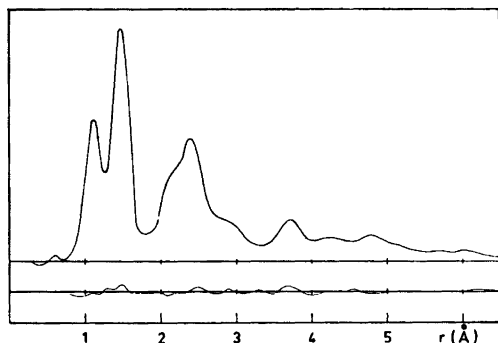


Fig. 2. Dipropyl ether. Experimental radial distribution curve. The lower curve shows the difference between the experimental values and the theoretical values for a conformational mixture of 26 % *aaaa* and 74 % *g±aag±* conformers. Artificial damping constant  $k=0.0020 \text{ \AA}$ .

0.25 mm of the photographic plate. Each plate was oscillated about the center of the diffraction diagrams and the intensity integrated over the arc. The data have been treated in the usual way.<sup>4</sup>

An empirical background has been subtracted on each plate before averaging the data. The molecular intensity curves from the 25 and the 58 cm nozzle-to-plate distances were scaled and combined to one experimental molecular intensity curve covering a scattering angle equivalent to  $s=1.5 \text{ \AA}^{-1}$  to  $s=30.25 \text{ \AA}^{-1}$  (Fig. 1). The mean values have been used in the overlap region. The intensities were modified by  $s/|f_C'|/|f_O'|$ , where  $|f'|$  is the complex scattering amplitude<sup>5,6</sup> for carbon and oxygen.

A least-squares procedure was used to refine the parameters estimated from the experimental radial distribution (RD) curve (Fig. 2). The calculations have been carried out on CDC 3300 and CDC 7400 (CYBER) computers.<sup>4</sup>

Table 1. Structure parameters for dipropyl ether obtained by least-squares refinement on the intensity data. Distances ( $r_a$ -values) are given in  $\text{\AA}$ , angles in degrees. The standard deviations given in parentheses have been corrected to take into account data correlation. The uncertainty arising from error in the electron wavelength is included. (For numbering system of the atoms see Fig. 3).

Conformation	B <i>aaaa</i>	C <i>ag±g±a</i>	D <i>g±aag±</i>	E <i>g±aag±</i>	F <i>aaaa</i>	G <i>aaag</i>
<b>Distances</b>						
O—C	1.404	1.404	1.404(4)	1.404	1.404(4)	1.404(6)
C—C	1.524	1.524	1.524(5)	1.524	1.524(5)	1.524(8)
C—H	1.116	1.116	1.116(4)	1.116	1.116(4)	1.116(6)
O...C(2)	2.390	2.380	2.390(10)	2.389	2.385(10)	2.391(17)
O...C(3)	} 3.763	} 3.740	} 3.036(22)	} 3.033	} 3.759(12)	} 3.762(20)
O...C(3)'						
C(1)...C(1)'	2.383	2.383	2.383(30)	2.383	2.383(28)	2.383(46)
C(2)...C(3)	2.551	2.525	2.536(13)	2.536	2.549(13)	2.548(20)
C(1)...C(2)'	3.697	} 2.983	} 3.697(12)	} 3.696	} 3.694(12)	} 3.698(18)
C(1)'\...C(2)	3.172					
C(1)...C(3)'	4.927	} 4.363	} 4.320(24)	} 4.371	} 4.925(31)	} 4.925(44)
C(1)'\...C(3)	4.516					
C(2)...C(2)'	4.424	3.901	4.762(31)	4.759	4.751(31)	4.764(52)
C(2)...C(3)'	5.874	} 5.004	} 5.174(41)	} 5.168	} 6.143(18)	} 5.231(81)
C(2)'\...C(3)	5.566					
C(3)...C(3)'	6.947	6.064	5.790(73)	5.124	7.454(31)	6.643(83)
<b>Angles</b>						
∠ COC	116.1	116.1	116.1(2.1)	116.1	116.1(2.1)	116.1(3.6)
∠ OCC	109.3	108.7	109.4(0.8)	109.2	109.1(0.8)	109.4(1.5)
∠ CCC	113.6	111.9	112.6(1.1)	112.1	112.6(1.1)	113.4(1.8)
∠ CCH(methyl)	114.7	114.7	114.7	114.7	114.7	114.7
∠ HCH(methylene)	108.0	108.0	108.0	108.0	108.0	108.0
$\beta$	90.3	} 72.4	0.0	0.0	0.0	0.0
$\beta'$	0.0		0.0	0.0	0.0	0.0
$\alpha$	0.0	0.0	} 72.1(2.9)	71.8	0.0	75.0(6.0)
$\alpha'$	0.0	0.0		-71.8	0.0	0.0

Table 2. Vibrational amplitudes ( $u$ -values) for dipropyl ether. The  $u$ -values are given in Å. The values are determined partly by trial and error, partly by refinements in separate cycles of a small number of parameters. Column I shows  $u$ -values for bond distances and distances over one angle, while column II and III show the  $u$ -values for *anti* and *gauche* distances, respectively.

Distances	I	II	III
O—C	0.043		
C—C	0.052		
C—H	0.070		
O···C(2)	0.063		
O···C(3)		} 0.098	} 0.110
O···C(3)'			
C(1)···C(1)'	0.069		
C(2)···C(3)	0.076		
C(1)···C(2)'		} 0.099	} 0.136
C(1)···C(2)'			
C(1)···C(3)'		} 0.114	} 0.139
C(1)'···C(3)'			
C(2)···C(2)'		0.113	0.140
C(2)···C(3)'		} 0.152	} 0.166
C(2)'···C(3)			
C(3)···C(3)'		0.200	0.221

## STRUCTURE ANALYSIS

Approximate values for the structure parameters used in the least-squares refinement are determined from the experimental RD curve in Fig. 2.

The first two peaks in the RD curve correspond to the bond distances in the molecule. The peak at about 1.1 Å represents the fourteen C—H distances which are assumed to be of equal length. The peak at 1.5 Å is composed of contributions from the C—O and C—C bond distances. A possible difference between the bond lengths of the terminal C—C bond and the C—C bonds within the chain cannot be determined from the experimental data. The refinement of one average C—C bond distance results in a bond length of 1.524 Å (Table 1)

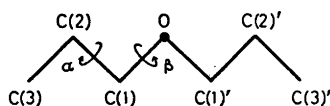


Fig. 3. Dipropyl ether. Model showing the numbering of the atoms and the torsion angles,  $\alpha$  and  $\beta$ .

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and a corresponding vibrational amplitude ( $u$ -value, Table 2) of 0.048 Å. From the magnitude of the  $u$ -value there is no indication of any change in the C—C bond length depending on position in the chain (Table 2).

The shoulder at about 2.1 Å represents non-bonded C···H and O···H distances. In the structure analyses it has been assumed that the plane through the hydrogen atoms in each methylene group is bisecting the CCC (OCC) valence angle. The largest contribution to the main peak at 2.4 Å comes from O···C and C···C distances over one angle. These broad peaks contain a large number of distances, many of these are contributing with about equal weight. However, large correlations between several distances and  $u$ -values make impossible the simultaneous refinement of the parameters. For this reason a great part of the vibrational amplitudes had to be adjusted by trial and error.

All the interatomic distances which are shorter than 2.6 Å, are independent of conformation. Fig. 4 reproduces the regions outside 2.6 Å in the theoretical RD curves, which show varying features dependent on the conformation of the dipropyl ether chain. In the structure analysis all *anti* conformations are fixed at exactly 180°, while the torsional angles of the *gauche* conformations are refined by a least-squares procedure.

The dipropyl ether chain may in principle have a number of different conformations depending on the torsion about the O—C(1), O—C(1)', C(1)—C(2) and C(1)′—C(2)′ bonds.

*aaaa*. The theoretical RD curve for the planar *aaaa* conformer (Fig. 4, curve F) shows two well-defined peaks, which are not present in the experimental RD curve. The area underneath the shoulder at about 3.0 Å is too small, while the peak at 3.7 is too large, due to the two O···C(3) and the two C(1)···C(2)′ distances at 3.76 and 3.69 Å. Also the area underneath the peak at 4.8 is too large, because the two C(1)···C(3)′ and the C(2)···C(2)′ are of approximately the same length. This also goes for the C(2)···C(3)′ distances at 6.1 Å in the all-*anti* conformer.

*aaag*. By rotating one of the methyl groups about the C(1)—C(2) bond (Fig. 4, curve G), a distribution of the interatomic distances is obtained which results in a fairly good agreement with the experimental curves. In this

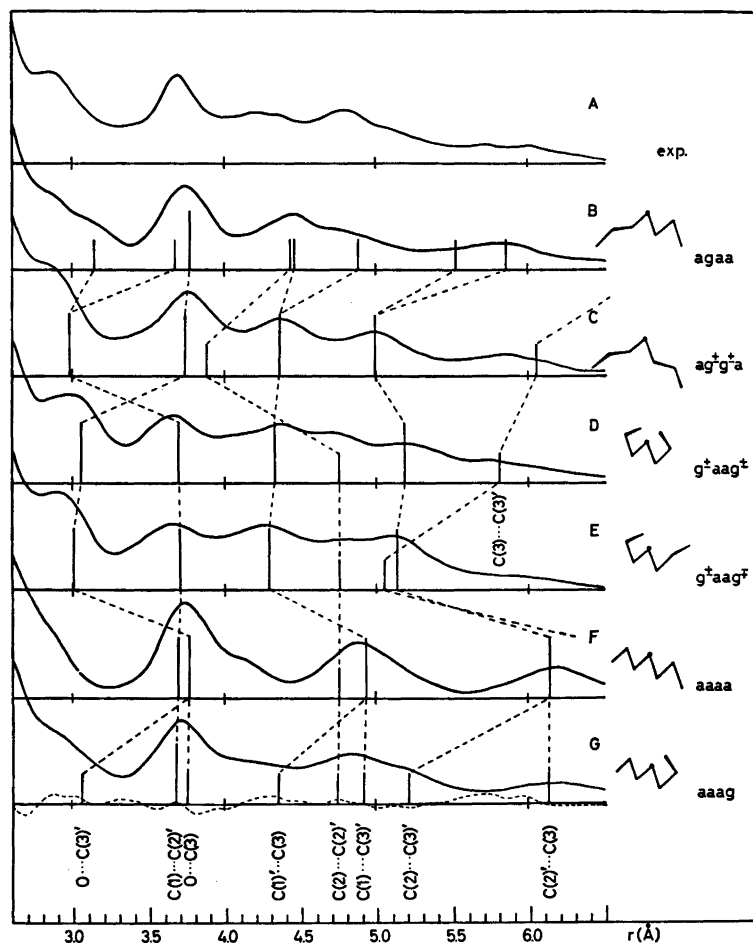


Fig. 4. Dipropyl ether. The outer part of the experimental (A) radial distribution curve compared with the corresponding part of the theoretical radial distribution curves for the conformers: *agaa* (B), *ag $\pm$ g $\pm$ a* (C), *g $\pm$ aag $\pm$*  (D), *g $\pm$ aag $\mp$*  (E), *aaaa* (F), and *aaag* (G). ( $k=0.0020$  Å).

conformer there could be one 1,4-CH $\cdots$ O *gauche* interaction.

*g $\pm$ aag $\pm$*  and *g $\pm$ aag $\mp$* . Further, equal rotation of both methyl groups about the C(1) $\cdots$ C(2) bonds results in a *g $\pm$ aag $\pm$*  or a *g $\pm$ aag $\mp$*  conformer. As may be seen from Table 1, the only pronounced difference in interatomic distances of these conformers is the length of the C(3) $\cdots$ C(3') distance, which is 5.79 Å in the former and 5.12 Å in the latter. This difference is shown in Fig. 4, curve D and E. None of these models, however, correspond satisfactorily to the experimental data. This means that two 1,4-*gauche* interactions between CH $_3$  and O can-

not be especially preferred, whether the methyl groups are on the same side or on opposite sides of the molecular plane.

*agaa*. Proceeding to the conformers arising from rotation about the O-C(1) bonds, the *agaa* conformer (Fig. 4, curve B) shows a theoretical RD curve, which is not in agreement with experimental data. The shoulder at 3.0 Å is too small due to the presence of only one C(1) $\cdots$ C(2') distance in this region, and the peak at 4.5 Å is too large due to the C(2) $\cdots$ C(2') and the C(1') $\cdots$ C(3) distances.

*ag $\pm$ g $\pm$ a*. By equal rotation about both O-C(1) and O-C(1')

at 3.0 Å in the RD curve will increase due to the shortening of the C(1)···C(2)' distance from 3.70 to 2.98 Å in agreement with the experimental RD curve. The area underneath the peak at 3.7 Å will, however, change very little as the loss of the C(1)···C(2)' distance in this region compared to the *agaa* conformer, will be compensated by the gain of the C(2)···C(2)' distance. The fact that the C(1)···C(3)' and C(1)'···C(3) distances are equal in an *ag±g±a* conformer, results in a too well-defined peak at 4.4 Å.

*ag±g±a*. This conformer can be disregarded because of the too short distances between the methylene groups C(2)H<sub>2</sub> and C(2)'H<sub>2</sub>.

As strong attractive 1,4-*gauche* CH···O interactions thus do not seem to be present in dipropyl ether, the molecule may well exist as an equilibrium mixture of more than one conformer. Based on the RD curves for the single conformations, theoretical radial distribution curves for mixtures of two conformations have been calculated. The bond distances, COC, CCH and HCH angles have been kept at fixed values during the refinement of the data and the CCC, OCC, the torsion angles, and the ratio of each conformer have been determined by a

least-squares procedure. Most of the single conformers have too large area underneath the peak at about 4.4 Å. Excepted are the *aaaa* conformer, which has a minimum in this region and the *aaag* conformer, which shows a fairly good agreement with experimental data. From this it might be expected that in the mixture of two conformers which gives the best fit to the experimental curve, one should be an *aaaa* conformer.

But as the *aaaa* conformer shows too large area at 3.7 Å and too small around 2.9 Å, the other conformer in the mixture must show the opposite effect in the mentioned regions (Fig. 5).

*aaaa* + *g±aag±*. The best agreement is obtained for a mixture of 26 % *aaaa* and 74 % *g±aag±* conformers. The peak at 3.0 Å which compared to the experimental data is too little for an all-*anti* conformer and too large for the *g±aag±* conformer, fits fairly well for the mixture of the two. A similar argument holds for the peak at 3.7 Å, while the lack of distances at 4.3 Å in the *aaaa* conformer is compensated for by C(1)···C(3)' distances in the *g±aag±* conformer. Taking into account the statistical population of the *gauche* conformer, the ratio

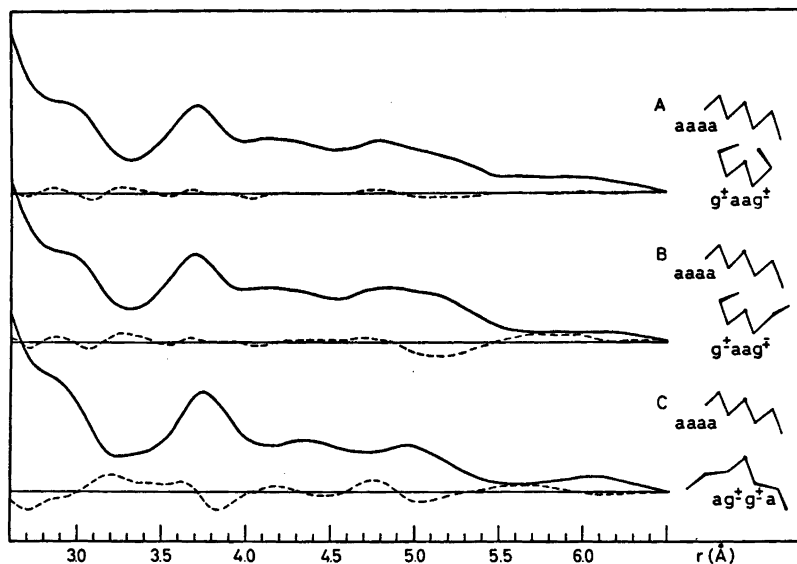


Fig. 5. Dipropyl ether. The outer part of the radial distribution curves for equilibrium mixtures of the conformers: 26 % *aaaa* + 74 % *g±aag±* (A), 28 % *aaaa* + 72 % *g±aag±* (B), and 18 % *aaaa* + 82 % *ag±g±a* (C). The broken lines show the difference between experimental and theoretical values. ( $k=0.0020$  Å).

$aaaa/g^{\pm}aag^{\pm}$  means that the energies of the two conformers are approximately equal. During the refinements the carbon-oxygen skeleton of the *anti* conformer is assumed to be exactly planar, while the  $\delta(\text{OCCO})$  of the  $g^{\pm}aag^{\pm}$  conformer is found to be  $72.1^{\circ}$  (Fig. 5, curve A).

$aaaa + g^{\pm}aag^{\mp}$ ,  $aaaa + ag^{\pm}g^{\pm}a$ . Curve B and C show the best fit between experimental and theoretical data obtained for mixtures of  $aaaa$  and  $g^{\pm}aag^{\mp}$  conformers (28 and 72 %, respectively) and for  $aaaa$  and  $ag^{\pm}g^{\pm}a$  conformers (18 and 82 %). The theoretical RD curve for the mixture of  $aaaa$  and  $ag^{\pm}g^{\pm}a$  conformers clearly shows larger deviations from the experimental data than the two other conformational mixtures shown in Fig. 5. By comparison of curve A and B it is seen that the somewhat larger discrepancies in the region 5.0–6.0 Å for the  $aaaa/g^{\pm}aag^{\mp}$  mixture compared to the  $aaaa/g^{\pm}aag^{\pm}$  mixture corresponds nicely to the position of the  $\text{C}(3)\cdots\text{C}(3')$  distance, which is 5.12 Å for the  $g^{\pm}aag^{\mp}$  conformer and 5.79 Å for the  $g^{\pm}aag^{\pm}$ . These circumstances indicate that if both methyl groups in dipropyl ether are in *gauche* positions to the oxygen atom, there may be a preference for one *gauche* interaction on each side of the oxygen atom rather than two on the same side. If the proportions in the conformational mixture were purely statistical, the ratio of the  $g^{\pm}aag^{\pm}$  conformer to the  $g^{\pm}aag^{\mp}$  should be 1:1, which does not seem to be the case for dipropyl ether.

## DISCUSSION

The conformational analysis of dipropyl ether in the gas phase does not result in an unequivocal solution of the problem. The only single conformation which gives a satisfactory agreement between theoretical and experimental data is the *aaag* conformer. However, a mixture of 26 %  $aaaa$  and 74 %  $g^{\pm}aag^{\pm}$  gives a good agreement and the smallest error of square residuals from the data refinement. Of course also a mixture of all three conformers will be an acceptable solution if the  $aaaa/g^{\pm}aag^{\pm}$  ratio is maintained. In that case, however, it is impossible to determine the ratio of the *aaag* conformer to the mixture, as both solutions fit satisfactorily to the experimental curves and so does any ratio between them.

As already mentioned, in larger ring systems<sup>1,2</sup> and polymer chains<sup>3</sup> built up of  $-(\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2)-$ units, all the dihedral angles  $\delta(\text{COCC})$  are found to be *anti* and all the  $\delta(\text{OCCC})$  *gauche*. This seems to favour a 1,4- $\text{CH}\cdots\text{O}$  *gauche* interaction. This favourable *gauche* interaction is also observed in other ethers.<sup>7,8</sup>

However, an NMR investigation of the conformations of aliphatic ethers by Dale *et al.*<sup>9</sup> concludes that the 1,4- $\text{CH}\cdots\text{O}$  *gauche* interaction in monoethers is not attractive. The effect of the 1,4- $\text{CH}\cdots\text{O}$  interaction is further explained as being attractive only when the interacting hydrogen atom has an acidic character. This is the case for hydrogen atoms bonded to carbon atoms in  $\alpha$ -position to oxygen. In unsubstituted monoethers the acidic character of the relevant hydrogen is missing, and the energy difference between *gauche* and *anti* conformers is found to be negligible.

It may be seen from Fig. 4 that a *gaag* conformer alone obviously does not give any satisfactory solution to the conformation problem of dipropyl ether. From this it may be concluded that there is no preference for 1,4- $\text{CH}\cdots\text{O}$  *gauche* interactions in this molecule and consequently the conformation is not comparable with the  $-(\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2)-$ units in larger ring systems and polymer chains, where all the dihedral angles  $\delta(\text{COCC})$  are *anti* and  $\delta(\text{OCCC})$  are *gauche*.

Based on the NMR results for monoethers,<sup>9</sup> it should be expected that dipropyl ether should not show attractive 1,4- $\text{CH}\cdots\text{O}$  *gauche* interactions, in good agreement with this investigation. On the other hand, the conformer distributions found here are not in agreement with the statistical distribution, and so there must be other effects resulting in an exclusion or very small portion of some conformers or a dominance of others. Thus, in the experimental data there is no support for conformations with *gauche* CCOC dihedral angles being present, and also indications of the absence of the  $g^{\pm}aag^{\mp}$  conformer.

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