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THE CONFORMATION OF NON-AROMATIC RING COMPOUNDS—XLIII[1]

CARBON-HALOGEN STRETCHING FREQUENCIES AND CONFORMATION OF 3-HALOGENO- AND *TRANS*-3,4-DIHALOGENOTETRAHYDROFURANS

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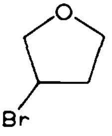
Abstract The IR and Raman spectra of 3-halogeno- and *trans*-3,4-dihalogenotetrahydrofurans were recorded. The conformations with the halogen atoms in axial position were found to predominate in solution, the substituents occupying the most puckered part of the ring. For the 3-halogeno compounds, this conclusion is confirmed by the dipole moments.

INTRODUCTION

In continuation of a series of studies on the conformation and geometry of halogenated cyclopentanes,[1–5] the present paper deals with the conformational properties of 3-bromo- (I), 3-chloro- (II), *trans*-3,4-dibromo- (III), *trans*-3-bromo-4-chloro- (IV) and *trans*-3,4-dichlorotetrahydrofuran (V), by means of dipole moments and IR and Raman spectra. Thus far, only a single study on the conformation of tetrahydrofurans has appeared in the literature. Gagnaire and Vottero[6] studied the conformation of some isomers of 2,5-dimethoxy-3,4-dibromotetrahydrofuran and of *trans*-2,5-dimethoxy-*cis*-3,4-dihydroxytetrahydrofuran. Reviews covering the literature on conformational analysis of the furanoid sugars are available.[7]



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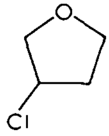

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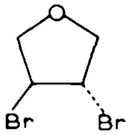

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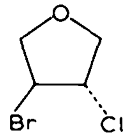

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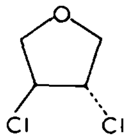

V

General principles

Like cyclopentane, the tetrahydrofuran (THF) ring is puckered.[8,9] However, the rotation of the puckering around the ring (pseudorotation[10]) is probably not free,[8] as in cyclopentane.[8,11] A potential energy barrier is assumed to occur because an O atom in planar arrangement is not seriously troubled by bond eclipsing. Pitzer and Donath[8] calculated a torsional barrier to pseudorotation in THF of 2·5 kcal/mole, using their model for cyclopentane (maximum torsional angle 48·1°). Recent X-ray data for a number of substituted furanoses[12] suggest that the THF ring is somewhat less puckered (maximum torsional angle 39°) and a reevaluation of the barrier opposing pseudorotation is therefore in order.* Figure 1 shows the most stable C_2 or half-chair[13] form and C_s or envelope[13] form for THF.

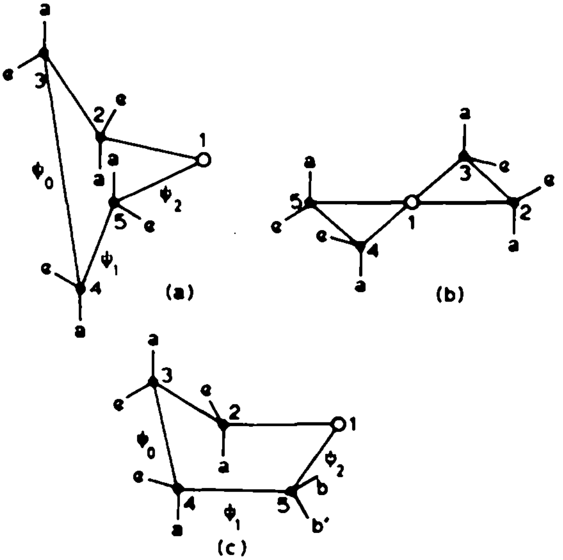

Fig. 1 Half-chair form in perspective (a), in projection (b) and envelope form (c) with axial, equatorial and bisectional valencies.

There is no *a priori* reason to assume that either of these basic conformations actually represents the most stable conformation in any given substituted THF. In order to describe these forms and all intermediate ones it is convenient to introduce a pseudorotation parameter Δ, which is called "the phase angle of pseudorotation".[10,14,15] Along the pseudorotation circuit, Δ varying from 0° to 720°, 10 C_s and 10 C_2 forms are met. If Δ is taken as zero for an arbitrary C_2 form, C_2 forms arise at $\Delta = 0°, 72°, 144°, \ldots$, etc. and C_s forms at $\Delta = 36°, 108°, 180°, \ldots$, etc. (cf. Figs 2 and 3). The C_2 forms at $\Delta = 0°$ and $\Delta = 360°$ are not identical, because an axial substituent in the former case has become equatorial in the latter and *vice versa*.

Introduction of substituents at C-3 and C-4 (Fig. 4) raises the barrier restricting pseudorotation still further. The barrier separates two energy minima which have different conformational characteristics (e.g. with equatorial and axial substituents) in the case of mono- and *trans*-disubstituted compounds. In each minimum, Δ may oscillate. We introduced the term *pseudolibration*[2] for this phenomenon. For 3-substituted tetrahydrofurans, 20 energetically different C_2 and C_s forms exist. For *trans*-3,4-disubstituted compounds, only 11 of the 20 forms are energetically different.

The calculation of the total torsional potential energy as a function of Δ has been carried out for 3-halogeno- and *trans*-3,4-dihalogenotetrahydrofurans according to the method described earlier.[2] Assuming a potential function of the type:

$$V_{ij} = \tfrac{1}{2}V^{\circ}_{ij}(1 + \cos 3\psi_{ij}) \qquad (1)$$

the following V° values are substituted:[8,16]

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* Recent studies[9] of the far IR spectrum of THF suggest that the barrier opposing pseudorotation is rather lower than thought previously.[8] However, further work on this problem must be awaited before it can be considered as settled definitively.

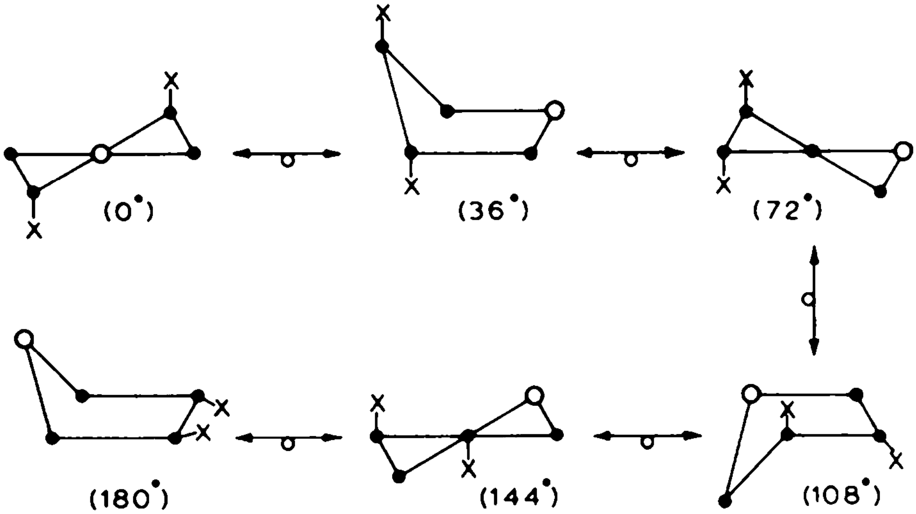

Fig. 2 Pseudorotation circuit between $\Delta = 0°$ and 180° for *trans*-3,4-dihalogeno-THF.

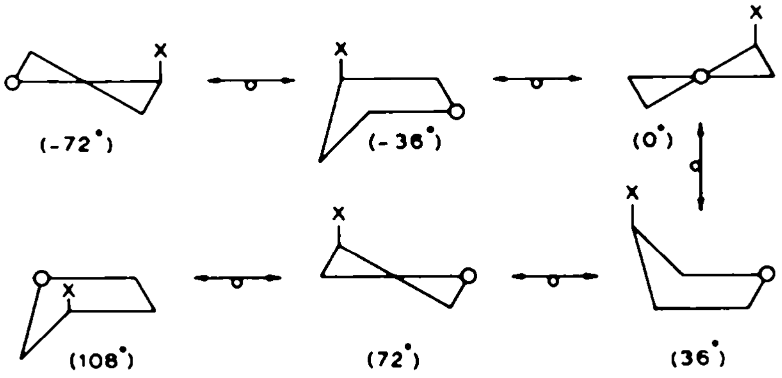

Fig. 3 Pseudorotation circuit between $\Delta = -72°$ and $+108°$ for 3-halogeno-THF.

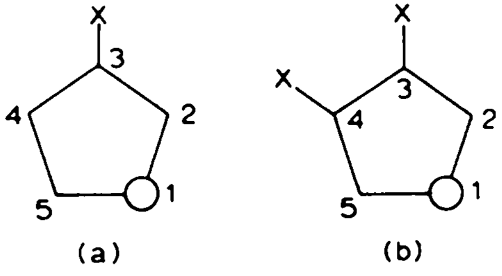

Fig. 4

CH_2—CH_2 = 2·8 kcal/mole (V_{45} in Fig. 4a)
CHX—CH_2 and CHX—CHX = 3·6 kcal/mole (V_{23} and V_{34} in Fig. 4a, V_{23}, V_{34} and V_{45} in Fig. 4b)
CH_2—O = 1·07 kcal/mole (V_{12} and V_{15} in Figs 4a and 4b).

For cyclopentane, the appropriate torsional angles ψ_{ij} can be calculated from the maximum torsional angle (ψ_m) for any value of Δ.[14,15] As a first approximation, this method can be applied to THF.* Taking $\psi_m = 39°$,[12] the torsional angles for the half-chair form depicted in Fig. 1a are: $\psi_0 = 39°$, $\psi_1 = 32°$, $\psi_2 = 12°$; for the envelope form (Fig. 1c): $\psi_0 = 37°$, $\psi_1 = 23°$, $\psi_2 = 0°$.

In Fig. 5 a plot of V against Δ is shown for the 3-halogeno- and *trans*-3,4-dihalogeno compounds.† Each dot represents one of the basic conformations depicted in Figs 2 and 3. Non-bonded and dipole–dipole interactions have not been included in these calculations, bond angle deformation was also neglected. However, it is expected that inclusion of these interactions will not change the general shape of the potential energy curve.[2] The following conclusions can be drawn:

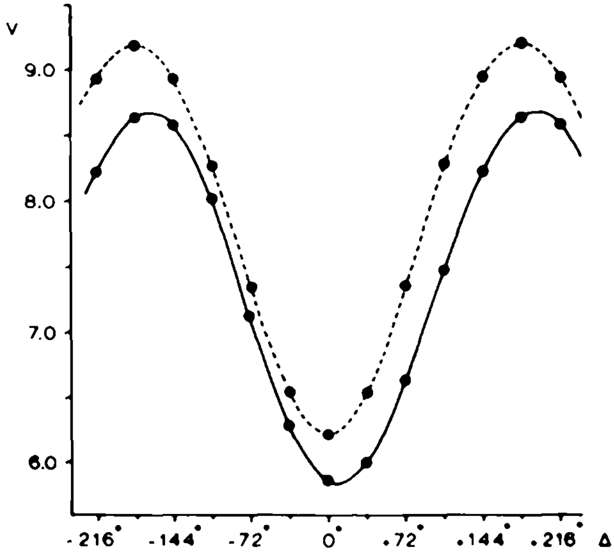

Fig. 5 The shape of the torsional barrier to pseudorotation in 3-halogeno-THF (full line) and in *trans*-3,4-dihalogeno-THF (dotted line). V in kcal/mole. $V_\Delta = V_{\Delta+360}$.

1. For the monohalogeno compounds the *torsional* energy minima correspond to the forms for which $\Delta = 10°$ (halogen axial) and $\Delta = 370°$ (halogen equatorial), so they do not correspond to one of the basic conformations. The minimum is 2·9 kcal/mole below the top of the barrier.

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* For cyclopentane, ψ_m is independent of Δ. The possibility that ψ_m varies with Δ for THF is neglected in the present approach. The relation between the five torsional angles ψ_j ($j = 0, 1, 2, 3, 4$) and Δ is then given by $\psi_j = \psi_m \cos(\frac{1}{2}\Delta + j\delta)$ with $\delta = 144°$.

† The calculations were carried out on the X1 computer by means of a program devised by H. J. Geise and B. Hesper.

2. For the *trans*-3,4-dihalogeno compounds, the *torsional* energy minima correspond to the symmetrical half-chair forms for which $\Delta = 0°$ (halogens axial) and $\Delta = 360°$ (halogens equatorial), 3·0 kcal/mole below the top.

3. For both classes of compounds, the conformations in which the halogen atom or atoms occupy the most puckered part of the ring and the oxygen atom occupies the planar part, are strongly preferred.

4. The energy wells of the tetrahydrofurans are steeper than those of the corresponding halogenocyclopentanes.[2] Hence, the amplitude of pseudolibration (i.e. the spreading in geometry of the conformations that contribute predominantly to the observed physical properties) is probably smaller in the former case than in the latter. This prediction is confirmed by our work on the IR and Raman spectra of chlorocyclopentane,[1] 3-chloro-THF, *trans*-1,2-dichlorocyclopentane[4] and *trans*-3,4-dichloro-THF (see below).

RESULTS

A. *IR and Raman spectra*

The IR and Raman spectra of compound III and the Raman spectrum of compound I are shown in Figs 6–8. Of special interest is the spectral range 500–800 cm^{-1}, where the carbon-halogen stretching vibrations occur. The C–Cl and C–Br stretching frequencies in aliphatic halogenides depend on the geometrical arrangement about the neighbouring C atoms. The single most essential factor seems to be the nature (C, H, halogen, O, etc.) of the atom or atoms anti to the halogen. By an extension of a notation introduced earlier,[17] an empirical set of parameters was derived[18] which allows the assignment of the C–Br and C–Cl stretching frequencies according to the chemical–geometrical combination. The chemical type of halogenide is specified by P (primary), S (secondary) and T (tertiary), the atom or atoms in anti-position are indicated by a subscript (H, C, O, X (halogen)). Data for various types of vibration are collected in Table I[18] (cf. also Ref. 19). The values presented in Table 1 are probably accurate to ±20 cm^{-1}.

TABLE 1. C–Br AND C–Cl STRETCHING FREQUENCIES FOR VARIOUS CHEMICAL–GEOMETRICAL COMBINATIONS

Type	C–Br (cm^{-1})	C–Cl (cm^{-1})
S_{HH}	535	611
S_{CH}	596	650
S_{XH}	596	650
S_{CC}	686	742
S_{CO}	728	767

(a) 3-*Halogenotetrahydrofurans.* The bands observed between 500 and 800 cm^{-1} are collected in Table 2.

The very strong bands found at 535 cm^{-1} for 3-bromo-THF and at 605 cm^{-1} for 3-chloro-THF can safely be assigned to the axial C-halogen stretching frequency (S_{HH} type); they agree very well with those found for the corresponding 3-halogenotetrahydropyrans[18,20] (535 and 595 cm^{-1}, respectively). These bands are by far the strongest of the spectrum.

The Raman spectra of bromo- and chlorocyclopentane show very strong bands with about the same frequencies as those for compounds I and II (514 and 590 cm^{-1}, respectively). These bands are also assigned to the axial C-halogen vibration.[1] The IR spectra of these compounds have been discussed,[21] but no definite assignment was made. The axial C–Cl stretching mode for chlorocyclopentane appears much broader than that for 3-chloro-THF, suggesting a larger amplitude of pseudolibration for the former compound. This is in agreement with the theoretical predictions.

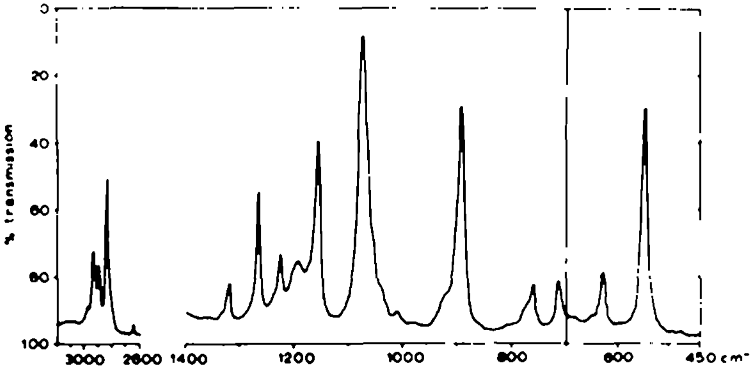

Fig. 6 Infrared spectrum of *trans*-3,4-dibromo-THF (solution in CS_2).

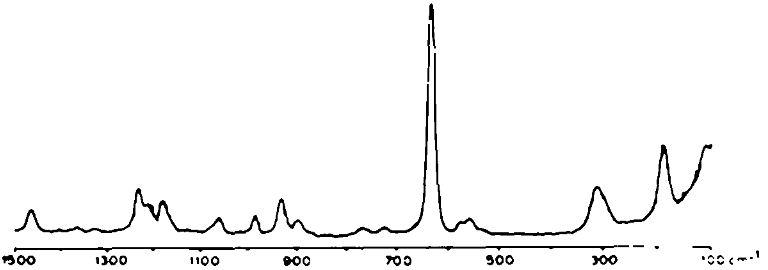

Fig. 7 Raman spectrum of *trans*-3,4-dibromo-THF (pure liquid).

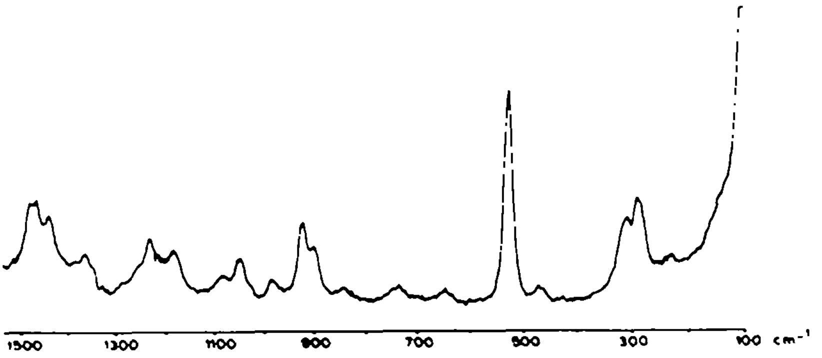

Fig. 8 Raman spectrum of 3-bromo-THF (pure liquid).

Table 2. IR and Raman spectra of 3-bromo- and 3-chloro-THF between 500 and 800 cm^{-1}

3-Bromo-THF (I)		3-Chloro-THF (II)	
IR (CS_2)	Raman (liq)	IR (CS_2)	Raman (liq)
535 (vs)	528 (vs)	605 (vs)	604 (vs)
655 (w)	650 (w)	667 (w)	665 (w)
740 (vw)	740 (vw)	758 (vw)	758 (vw)
		795 (vw)	795 (vw)

The assignment of the equatorial C-halogen stretching frequency (S_{CO} type) is more difficult. The weak bands at 655 cm^{-1} (compound I) and at 667 cm^{-1} (compound II) probably correspond to a band at 654 cm^{-1} in the spectrum of THF,[22,23] which is assigned to a CH_2 rocking mode.[23] The very weak bands at 740 cm^{-1} (compound I) and at 758 cm^{-1} (compound II) may be due to the equatorial C–X vibration; they agree rather well with the S_{CO} frequencies (cf. Table 1) and with the equatorial C–X frequencies for the corresponding 3-halogenotetrahydropyrans[20] (720 and 760 cm^{-1}, respectively). However, the spectrum of THF itself shows bands at 725 and 761 cm^{-1}.[22,23] Thus, the assignment is not conclusive, but it is clear that the equatorial conformation, if present at all, is hardly detectable. We conclude that the axial form predominates to a surprisingly large extent, which is in accord with the dipole moments of these compounds (see section B). The results of the above discussion are summarized in Table 3.

Table 3. Carbon-halogen stretching frequencies (IR values in cm^{-1}) in 3-halogenotetrahydrofurans and -tetrahydropyrans,[20] compared with the empirical values given in Table 1

Compound or type	Axial C–X str.	Equatorial C–X str.
S_{HH} (bromo)	535	
S_{CO} (bromo)		728
3-Bromotetrahydrofuran	535	740?
3-Bromotetrahydropyran	535	720
S_{HH} (chloro)	611	
S_{CO} (chloro)		767
3-Chlorotetrahydrofuran	605	758?
3-Chlorotetrahydropyran	595	760

(b) trans-3,4-*Dihalogenotetrahydrofurans.* The IR and Raman bands between 500 and 800 cm^{-1} for compounds III–V are presented in Table 4.

Consider the strong bands displayed by the dibromo compound III:

(a) A very strong Raman active band at 632 cm^{-1}, which is weak in the IR spectrum.

(b) A weak Raman band at 558 cm^{-1}, which is very strong in the IR spectrum.

This combination of bands is highly characteristic of an approximately antiplanar

TABLE 4. IR AND RAMAN SPECTRA OF *trans*-3,4-DIBROMO- (III), *trans*-3-BROMO-4-CHLORO- (IV) AND *trans*-3,4-DICHLORO-THF (V) BETWEEN 500 AND 800 cm^{-1}

III		IV		V	
IR (CS_2)	Raman (liq)	IR (CS_2)	Raman (liq)	IR (CS_2)	Raman (liq)
558 (vs)	558 (8)	598 (vs)	597 (34)	663 (vs)	660 (sh)
632 (w)	632 (100)	673 (m)	672 (100)	688 (sh)	687 (vs)
715 (w)	724 (4)	722[*] (w)	724 (6)	721[*] (w)	721 (w)
761 (w)	769 (4)	768[*] (w)	775 (6)	772[*] (w)	768 (w)

[*] From the spectrum of the neat liquid.

arrangement of the X–C–C–X system (X = Cl or Br);[4,18,24] evidence has been accumulated from about fifty compounds, including 5- and 6-membered rings and open-chain compounds. The two bands are therefore assigned to the strongly coupled C–Br stretching vibrations of the diaxial conformation (S_{HX} type), the Raman active vibration being due to the symmetrical mode and the strong IR band originating from the asymmetrical mode. The analogous *aa* bands in the bromochloro IV and in the dichlorocompound V obey the same intensity rule and are similarly assigned. The axial C-halogen stretching frequencies for compounds III–V are compared with those for the corresponding cyclopentanes,[4] tetrahydropyrans[20] and cyclohexanes[18,24] in Table 5.

TABLE 5. AXIAL C-HALOGEN STRETCHING FREQUENCIES (IR VALUES IN cm^{-1}) IN *trans*-3,4-DIHALOGENO-TETRAHYDROFURANS AND -TETRAHYDROPYRANS,[20] *trans*-1,2-DIHALOGENOCYCLOPENTANES[4] AND -CYCLOHEXANES[18,24] COMPARED WITH THE VALUES GIVEN IN TABLE 1.

Compound or type	Symm. C–X str.	Asymm. C X str.	Average	$\Delta\nu$
S_{HX} (bromo)			596	
trans-3,4-Dibromo-THF	632	558	595	74
trans-1,2-Dibromocyclopentane	607	542	575	65
trans-3,4-Dibromo-THP	665	555	610	110
trans-1,2-Dibromocyclohexane	653	542	597	111
S_{HX} (bromochloro)			623	
trans-3-Bromo-4-chloro-THF	673	598	635	75
trans-1-Bromo-2-chlorocyclopentane	650	582	616	68
trans-1-Bromo-2-chlorocyclohexane	665	580	623	85
S_{HX} (chloro)			650	
trans-3,4-Dichloro-THF	688	663	675	25
trans-1,2-Dichlorocyclopentane	688	652	670	36
trans-3,4-Dichloro-THP	715	647	681	68
trans-1,2-Dichlorocyclohexane	690	610	650	80

From Table 5 it is seen that the characteristic frequency difference $\Delta\nu = \nu_{symm} - \nu_{asymm}$ is definitely smaller in the 5-membered than in the 6-membered ring compounds, especially for the dichlorides. As this very low value for $\Delta\nu$ is also found for *trans*-1,2-dichloroindan[25] (28 cm^{-1}), it seems to be characteristic of *vic*. axial dichlorides of 5-membered rings.

As the C–X stretching bands of *trans*-1,2-dichlorocyclopentane appear very broad and diffuse, we suggested[4] that this compound exhibits appreciable pseudolibration. For *trans*-3,4-dichloro-THF these bands appear sharp, suggesting that the energy well for the former compound is much less deep than for the latter (Fig. 5).

Carbon-halogen bands due to the *ee* conformation (S_{CO} type) appear to be absent in the spectra. The weak bands appearing at about 720 and 770 cm^{-1} in the spectra of compounds III–V are not ascribed to the equatorial C–X vibrations; no shift to higher frequency is observed in the series BrBr → BrCl → ClCl. Besides, THF itself[22,23] shows bands at 725 and 761 cm^{-1}. Thus, the diaxial conformation should predominate to an extent of at least 90%.

B. *Dipole moments*

The dipole moments have been measured in benzene and in carbon tetrachloride at 25° (Table 6).

TABLE 6. DIPOLE MOMENTS (D) OF COMPOUNDS I–V IN BENZENE AND IN CARBON TETRACHLORIDE AT 25°

Compound	μ (C_6H_6)	μ (CCl_4)
3-Bromo-THF (I)	2·11	2·03
3-Chloro-THF (II)	2·16	2·10
trans-3,4-Dibromo-THF (III)	1·07	1·07
trans-3-Bromo-4-chloro-THF (IV)	1·01	1·01
trans-3,4-Dichloro-THF (V)	1·03	1·05

The estimated dipole moments of the AA and EE conformers of the dihalogenides, based on the following partial moments (Fig. 9): $\mu_1 \sim 1{\cdot}5$ D, $\mu_2 \sim 0{\cdot}5$ D, $\mu_3 \sim 2{\cdot}7$–3 D, are: $\mu_{AA} = 1$ D, $\mu_{EE} = 1{\cdot}2$–$1{\cdot}5$ D. As the difference between these moments is very small, no definite conclusions can be drawn as to the conformer distribution of compounds III–V.

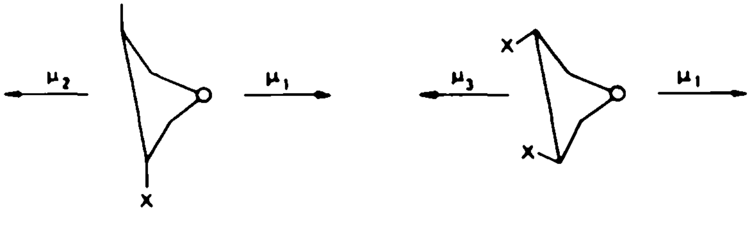

FIG. 9.

Calculation of the dipole moments of the conformers of the monohalogenides, taking the partial C–X moment equal to 2·0–2·1 D and the C–O–C moment equal to 1·5 D, yields: $\mu_A = 2{\cdot}15 \pm 0{\cdot}1$ D, $\mu_E = 1{\cdot}45 \pm 0{\cdot}1$ D. Thus, it is clear from the dipole moments measured for compounds I and II that the axial form of the 3-halogenotetrahydrofurans predominates to a large extent, in accord with the conclusions drawn from the vibration spectra (section A).

CONCLUSION

The vibration spectra and dipole moments of the 3-halogeno- and *trans*-3,4-dihalogenotetrahydrofurans indicate that the axial conformations predominate in solution. This strong preference for axial forms is also shown by the corresponding cyclopentanes.[1, 3, 4] It is noteworthy that with the corresponding 3-halogeno- and *trans*-3,4-dihalogenotetrahydropyrans[20] the equatorial conformers are predominant. The halogenated tetrahydrofurans are expected to be less flexible than the halogenocyclopentanes, which is confirmed by the appearance of the carbon-halogen stretching modes.

EXPERIMENTAL

Syntheses

3-*Bromo-THF* (I) was prepared by a method described[26] for the synthesis of 2-chloroindan from 2-indanol. 20 g 3-hydroxy-THF (Fluka, n_D^{25} 1·4482) was converted into the corresponding tosylate with 55 g tosyl chloride in 71 g pyridine. The tosylate was stirred with 76 g dry LiBr in 300 ml diethylene glycol for 8 hr at 100°. 650 ml water was added and the mixture was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent was removed at diminished pressure. Fractionation of the residue yielded 3-bromo-THF, b.p. 48°/10 mm; n_D^{25} 1·4913 (Lit.[27] b.p. 49°/11 mm; n_D^{25} 1·4912). (Found: Br, 51·9. Calc. for C_4H_7OBr (151·01): Br, 52·9%).

3-*Chloro-THF* (II) was prepared from the tosylate of 3-hydroxy-THF and LiCl by the method described for I; b.p. 35° 10 mm; n_D^{20} 1·4530 (Lit.[28, 29] b.p. 59–61° 30 mm; n_D^{20} 1·4530). (Found: Cl, 33·1 Calc for C_4H_7OCl (106·55): Cl, 33·3%).

trans-3,4-*Dibromo-THF* (III) was obtained by the addition of Br_2 to 2,5-dihydrofuran in CH_2Cl_2 at −20°; b.p. 85°/15 mm; n_D^{20} 1·5565 (Lit.[30] b.p. 80–83°/10 mm; n_D^{21} 1·5502). (Found: Br, 69·9. Calc. for $C_4H_6OBr_2$(229·91): Br, 69·5%).

trans-3-Bromo-4-chloro-THF (IV) was prepared from 2,5-dihydrofuran and N-bromosuccinimide–HCl in CH_2Cl_2 by the procedure described;[31] b.p. 69°/15 mm; n_D^{20} 1·5200. (Found: halogen 61·8. Calc. for C_4H_6OBrCl (185·45): halogen 62·2%).

trans-3,4-*Dichloro-THF* (V) was obtained by chlorinating 2,5-dihydrofuran employing SO_2Cl_2 according to the method described,[32] b.p. 52°/15 mm; n_D^{20} 1·4811 (Lit.[33] b.p. 85 86°/63 mm; n_D 1·4821 (temp not stated)). (Found: Cl, 50·1. Calc. for $C_4H_6OCl_2$ (141·00): Cl, 50·3%).

The purity of the compounds was also checked by means of the 60 Mc/s NMR spectra. An analysis of the spectra was not possible on account of their complexity.

Dielectric measurements

The electric moments were determined by measuring dielectric constants and densities of 5 or 6 solns of each compound in benzene and in carbon tetrachloride (molar fraction range 0–0·02) at 25° as described.[3] The total polarization P_{20} was calculated by the method of Halverstadt and Kumler;[34] the dipole moments followed from

$$\mu = 0{\cdot}01281 \times 10^{-18}[(P_{20} - R_D)\,T]^{\frac{1}{2}}$$

The infrared spectra were obtained with a Unicam double beam spectrophotometer (SP 100). The spectra were taken from solutions (~30 mg/ml) in carbon disulfide, and from the neat liquids. The wave numbers in the range 400–1500 cm^{-1} in CS_2 are presented below.

TABLE 7. NUMERICAL DATA OF THE MEASUREMENTS OF THE DIPOLE MOMENTS

Compound	Solvent*	α	β	P_{20}	R_D	μ
I	T	5·182	+0·000	112·01	27·98	2·03
	B	6·169	−1·001	118·67	27·98	2·11
II	T	5·444	+0·161	115·21	25·10	2·10
	B	6·337	−0·372	120·53	25·10	2·16
III	T	1·682	−0·233	59·16	35·70	1·07
	B	1·728	−1·916	59·27	35·70	1·07
IV	T	1·377	−0·069	53·43	32·82	1·01
	B	1·397	−1·305	53·53	32·82	1·01
V	T	1·354	+0·099	52·40	29·94	1·05
	B	1·375	−0·728	51·42	29·94	1·03

* T = carbon tetrachloride, B = benzene.

3-*Bromo-THF* (I): 535 (vs), 655 (w), 740 (vw), 842 (w), 902 (sh), 920 (vs), 970 (sh), 1052 (vs), 1085 (vs), 1180 (m), 1230 (s), 1255 (sh), 1326 (vw), 1360 (vw), 1438* (m,b).

3-Chloro-THF (II): 605 (vs), 667 (w), 758 (vw), 795 (vw), 848 (w), 904 (vs), 928 (sh), 975 (sh), 1065 (vs), 1088 (vs), 1192 (w), 1215 (w), 1250 (sh), 1265 (s), 1330 (w), 1443* (b,m).

trans-3,4-Dibromo-THF (III): 558 (vs), 632 (w), 715 (w), 761 (w), 897 (s), 923 (sh), 981 (vw), 1013 (vw), 1042 (sh), 1080 (vs), 1158 (s), 1193 (w), 1227 (w), 1268 (m), 1320 (w), 1458* (m), 1465* (m).

trans-3-Bromo-4-chloro-THF (IV): 598 (vs), 673 (m), 722* (w), 768* (w), 900 (vs), 928 (sh), 974 (vw), 994 (vw), 1016 (vw), 1058 (vs), 1170 (m), 1195 (m), 1216 (sh), 1242 (w), 1273 (m), 1322 (w), 1468* (m,d).

trans-3,4-Dichloro-THF (V): 663 (vs), 688 (sh), 721* (w), 772* (w), 823* (w), 848* (w), 900 (vs), 932 (sh), 972 (vw), 1001 (vw), 1019 (w), 1084 (vs), 1110 (sh), 1185 (sh), 1206 (s), 1255 (w), 1276 (m), 1322 (w), 1460* (m), 1467* (m).

The Raman spectra were recorded on a photoelectric Hilger and Watts Ramanspectrometer with scanning attachment. Data on the performance of this apparatus have been given elsewhere.[35] The spectra were taken from the neat liquids with slit widths corresponding to 10 cm^{-1}, scanning speed 1 cm^{-1}sec^{-1}, time constant 2·5 sec. The frequencies in cm^{-1} between 200 and 1500 cm^{-1} are presented with the measured peak intensities on the usual relative scale (intensity of the strongest line = 100).

3-Bromo-THF (I): 290 (38), 312 (32), 528 (100), 650 (w), 740 (vw), 845 (w), 902 (sh), 920 (38), 982 (w), 1045 (20), 1082 (w), 1180 (22), 1230 (25), 1326 (vw), 1364 (w), 1436 (28), 1470 (35).

3-Chloro-THF (II): 336 (sh), 362 (60), 604 (100), 665 (20), 758 (vw), 795 (vw), 850 (vw), 906 (sh), 932 (95), 988 (20), 1060 (35), 1090 (15), 1218 (55, vb), 1248 (sh,b), 1336 (vw), 1365 (vw), 1440 (sh), 1465 (45).

trans-3,4-Dibromo-THF (III): 311 (18,b), 558 (8), 632 (100), 724 (4), 769 (4), 897 (7), 933 (16), 986 (8), 1013 (vw), 1062 (7), 1180 (13), 1213 (sh), 1233 (18), 1327 (vw), 1365 (vw), 1465 (9).

trans-3-Bromo-4-Chloro-THF (IV): 240 (34), 302 (24), 353 (31), 597 (34), 672 (100), 724 (6), 775 (6), 898 (18), 935 (32), 990 (21), 1061 (15), 1175 (24), 1222 (12), 1247 (31), 1330 (w), 1362 (w), 1466 (24).

trans-3,4-Dichloro-THF (V): 203 (b,w), 266 (22), 342 (sh), 370 (52), 660 (sh), 687 (100), 721 (w), 768 (w), 897 (20), 935 (32), 998 (23), 1062 (18), 1198 (20), 1220 (24), 1258 (20), 1326 (w), 1362 (w), 1463 (27).

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* From the spectrum of the neat liquid.

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