

Intramolecular OH $\cdots\pi$ Interaction. II. The Molecular Structure and Conformation of 4-Pentyn-1-ol

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The molecular structure and conformational composition of 4-pentyn-1-ol have been studied by gas-phase electron diffraction. The results of normal coordinate analyses and molecular mechanics (MM2) calculations for the various conformers are described. The conformational mixture was found to be dominated by the only conformer having the OH group and the C \equiv C bond close enough for OH $\cdots\pi$ interactions to occur.

IR spectra of the title compound have been recorded under various conditions, and O–H absorption bands corresponding to a free O–H group as well as to an intramolecularly hydrogen-bonded O–H group have been observed.

Dedicated to Professor Otto Bastiansen on his 70th birthday

The phenomenon of intramolecular hydrogen bonding has been extensively investigated in many laboratories, primarily through the use of infrared spectroscopy.^{1,2} Studies of the effects of OH $\cdots\pi$ hydrogen bonding^{3–7} have, however, been rather limited.

In recent years, molecules influenced by intramolecular OH $\cdots\pi$ hydrogen bonding have also been investigated by other methods, such as microwave spectroscopy,^{8–11} NMR,^{12,13} gas-phase electron diffraction (GED)^{14,15} and X-ray diffraction.¹⁶ Studies of intramolecular OH $\cdots\pi$ hydrogen bonding have mainly been concentrated on molecules with limited conformational freedom and with geometries in which an OH group and a π system are forced to be close to one another.

The present investigation forms part of a wider study of possible intramolecular OH $\cdots\pi$ hydrogen bonding in molecules with a high degree of conformational freedom and where conformers with an OH group and a π system close to each other are expected to give only minor contributions, unless attractive forces between the two groups exist.

The conformational distribution in 4-pentyn-1-ol was recently studied by GED.¹⁵ Fourteen

conformers differing in C¹–C² (*anti*/ \pm *gauche*), C²–C³ (*anti*/ \pm *gauche*) and C³–C⁴ (*syn*/ \pm *skew*) dihedral angles were considered. The study showed that the 4-pentyn-1-ol gas conformational mixture was dominated by the only conformer having the OH group and the C=C bond close enough for intramolecular OH $\cdots\pi$ interactions to occur. Molecular Mechanics calculations (MM2), which do not take possible OH $\cdots\pi$ interactions into account, predicted this conformer to contribute by only 6.6 %. These results do indeed therefore indicate that attractive OH $\cdots\pi$ interactions are strong enough to be of major importance in determining the conformational behaviour of the free molecules.

4-Pentyn-1-ol (in the following referred to as pentynol) has – due to the linearity of the triple bond moiety – one torsional degree of freedom less than 4-pentyn-1-ol. The conformational properties associated with the pentynol molecule are therefore considerably simpler than those for the latter compound. The molecule has, however, large enough conformational freedom to be very well suited for elucidating the possible influence of attractive OH $\cdots\pi$ interactions.

Molecular mechanics calculations

Molecular mechanics calculations were carried out for fourteen different conformers of pentynol, using Allinger's MM2 program.¹⁷ The conformers differ primarily in the magnitudes of the C²-C³, C¹-C² and C-O dihedral angles. The results are presented in Table 1.

If the C-O dihedral angle is not taken into account, the conformational problem is reduced from encompassing fourteen to only five conformers (Fig. 1). From Table 1 it will be seen that, for all combinations of the C²-C³ and C¹-C² dihedral angles, the calculated energy is lowest for an *anti* C-O dihedral angle. The calculated energies, adjusted for the lower entropy of conformer AAA, have been used for estimating the conformational composition. The calculated contributions for the AA, AG, GA, GG and G⁺G⁻ [$\Theta(\text{C}^2-\text{C}^3)$; $\Theta(\text{C}^1-\text{C}^2)$] conformers are presented in Table 1. The percentage contributions are calculated taking all fourteen conformers into consideration, as well as by including only the five conformers with an *anti* C-O dihedral angle. The latter results are given in brackets.

The calculations show that the omission of conformers with a *gauche* C-O dihedral angle does

not seriously influence the calculated conformational composition.

The calculations described above are of importance for the electron diffraction study of the conformational composition of pentynol, because the position of the hydroxyl hydrogen atom cannot be expected to be well determined by GED, especially when several conformers may be involved. The MM2 calculations show that no serious errors are introduced if pentynol is treated as a mixture of five conformers differing in the C²-C³ and C¹-C² dihedral angles.

Experimental

A commercial sample of 4-pentyn-1-ol from ICN Life Science Group, K&K, was used in the present study.

Electron diffraction diagrams were recorded on the Oslo apparatus¹⁸ with nozzle-to-plate distances of 485.21 (4 plates) and 205.21 mm (5 plates). Kodak Electron Image photographic plates were used, the nozzle-tip temperature being 72°C for the long and 78°C for the short nozzle-to-plate distance. The electron wavelength was 0.06463 Å, as calibrated against diffraction patterns for gaseous benzene using $r_s(\text{C}-\text{C}) = 1.3975 \text{ \AA}$ as a standard. The esti-

Table 1. Results from molecular mechanics (MM2) calculations for various conformers of 4-pentyn-1-ol (angles in degrees, energies in kcal/mol).

Conformer ^a	$\Theta(\text{C}^2-\text{C}^3)$	$\Theta(\text{C}^1-\text{C}^2)$	$\Theta(\text{C}-\text{O})$	$\angle\text{C}_3$	$\angle\text{C}_2$	$\angle\text{C}_1$	<i>E</i>	ΔE	% Contr. ^b
AAA	180.0	180.0	180.0	111.4	111.4	108.8	1.736	0.0	17.4 (16.4) AA
AAG	179.9	179.9	69.2	111.3	111.4	109.4	2.241	0.505	
AGA	178.3	62.2	179.4	111.2	112.3	109.2	1.912	0.176	23.4 (24.5) AG
AGG	179.4	61.7	70.0	111.2	112.3	109.7	2.427	0.691	
AG ⁺ G ⁻	177.3	64.0	-83.2	111.3	112.6	109.8	2.750	1.014	
GAA	64.8	178.1	179.3	111.9	112.5	108.7	1.791	0.055	30.4 (30.1) GA
GAG	65.2	177.7	70.6	111.8	112.4	109.3	2.293	0.557	
G ⁺ AG ⁻	64.8	179.0	-70.4	112.0	112.4	109.3	2.426	0.690	
GGA	63.9	61.1	181.1	111.9	113.3	109.2	2.011	0.275	19.4 (20.9) GG
GGG	64.3	60.3	70.9	112.0	113.3	109.8	2.696	0.960	
G ⁺ G ⁺ G ⁻	61.2	60.4	-85.3	111.9	113.6	109.8	2.689	0.953	
G ⁺ G ⁻ A	68.4	-67.0	178.9	113.6	112.8	109.6	2.580	0.844	9.4 (8.1) G ⁺ G ⁻
G ⁺ G ⁻ G ⁺	70.5	-68.5	83.0	112.8	114.0	110.3	3.001	1.265	
G ⁺ G ⁻ G ⁻	69.5	-63.7	-63.8	112.5	113.7	110.4	2.935	1.199	

^aThe conformational assignments refer to the C²-C³/C¹-C²/C-O dihedral angles. ^bThe numbers in brackets refer to the calculated conformational composition when only the five conformers with $\Theta(\text{C}-\text{O}) = 180^\circ(\text{A})$ are considered.

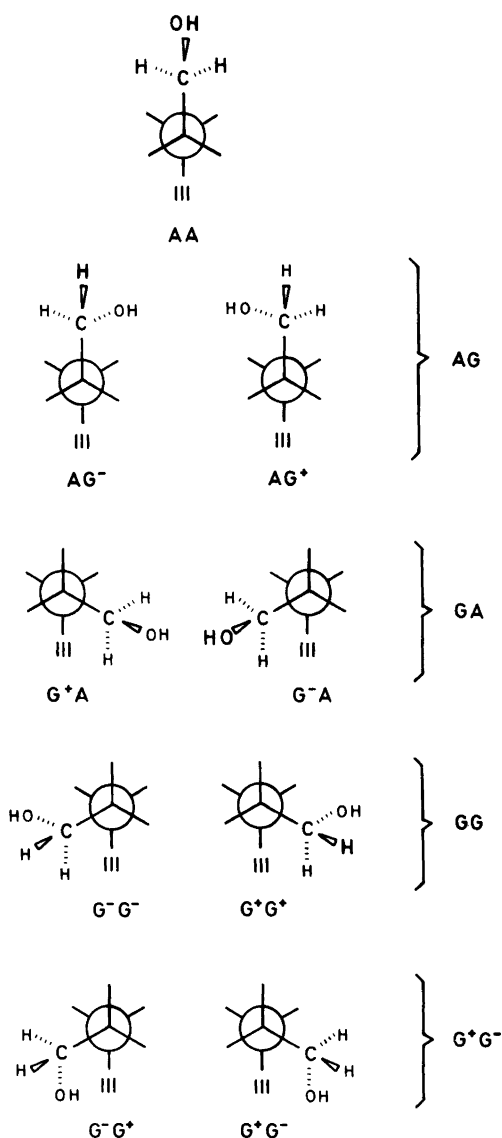


Fig. 1. Schematic representations of the pentynol conformers considered in the present study.

mated standard deviation in the determination of the wavelength is 0.1%. Ranges of data were 1.500–16.500 ($\Delta s = 0.125$) and 6.25–35.00 ($\Delta s = 0.25$) \AA^{-1} .

The experimental data were processed in the usual way.¹⁹ The intensities were modified by $s|f'_c|^{-2}$, and the scattering amplitudes (f') were calculated by the partial-wave method,²⁰ using

Hartree-Fock potentials for the C and O atoms²¹ and the best electron density of bonded hydrogen for the H atoms.²² The inelastic scattering factors used were those of Tavard *et al.*²³

IR- spectra of pentynol were recorded under the following conditions: *gas spectra*: heatable gas cell, 10 cm path length; *solution spectra*: solvents: CCl_4 and CS_2 ; Cell thicknesses: 10 mm and 1 mm; *pure liquid*: as capillary film.

Structure analysis

The molecular structure and conformational composition of pentynol were determined from least-squares refinements of the molecular intensity data, in combination with information obtained from radial distribution (RD) curves.

Root-mean-square amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K) were calculated²⁴ for the AAA, AGA, GAA, GGA, G^+G^-A and $G^+G^-G^+$ conformers of pentynol, and were applied throughout the study. The three-letter conformational assignments refer to the C^2-C^3 , C^1-C^2 and $C-O$ dihedral angles (when, in the following, a conformer is represented by a two-letter symbol, this refers to the C^2-C^3 and C^1-C^2 dihedral angles). The calculated vibrational amplitudes for the non-bonded $C\cdots C$ and $C\cdots O$ distances of the five conformers that have been studied are shown in Table 2. Some of the vibrational amplitudes differ by a factor of 3 from one conformer to another. This demonstrates the necessity of calculating the vibrational quantities for each of the various possible conformers.

The geometries of the pentynol conformers were based on r_a molecular models, which include corrections for shrinkage effects.²⁵

The internuclear distances in the pentynol conformers differ primarily in the outer r region ($r > 2.5$ \AA). This is demonstrated in Fig. 3, which shows the outer part of the theoretical RD curves for each of the considered pentynol conformers, with the experimental RD curve stippled in. The large experimental area centered at 3.0 \AA is most likely due to 1,4 $C\cdots C$ and $C\cdots O$ *gauche* distances (see Table 3), and indicates a substantial contribution from GG and/or G^+G^- conformers. The shape of the peak at ca. 2.5 \AA does, however, clearly favour the latter (see Fig. 3).

The MM2 calculations indicate a total contribution from the three G^+G^- conformers

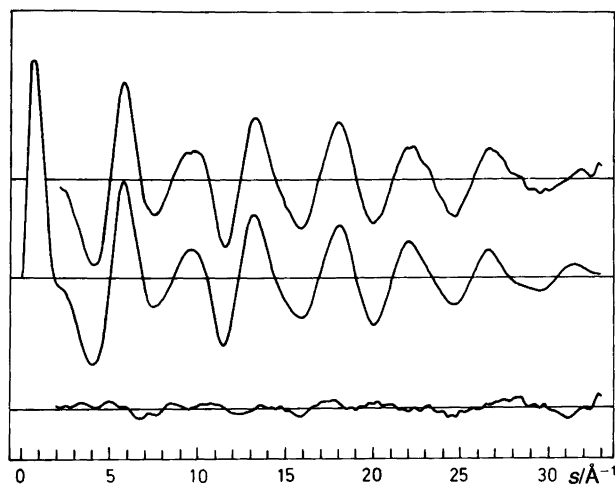


Fig. 2. Experimental and theoretical molecular intensities for pentynol, together with the difference curve. The theoretical curve is calculated for the final model (Table 4).

(G^+G^-A , $G^+G^-G^+$, $G^+G^-G^-$) of less than 10%. An eventual increase in the total G^+G^- contribution will probably be due to an increase in the $G^+G^-G^+$ conformer population as a result of stabilization by attractive $OH\cdots\pi$ interactions. It therefore seemed reasonable to let the $G^+G^-G^+$ conformer represent the total G^+G^- contribution when the conformational composition is being modelled. The four other conformers included in the conformational model (AA, AG, GA, GG) all have *anti* C–O dihedral angles, in accordance with the calculated MM2 steric energy minimum for each of these groups.

A single pentynol conformer is defined by fifteen geometrical parameters (Table 4) when linearity of the triple-bond moiety is assumed, as well as equality of the $C_{sp^3}-H$ bonds, the $C_{sp^3}-C_{sp^3}$ bonds and the H–C–H angles. Five pentynol conformers have been considered for the conformational mixture, and it is clearly not possible to determine geometrical parameters for all of these individually.

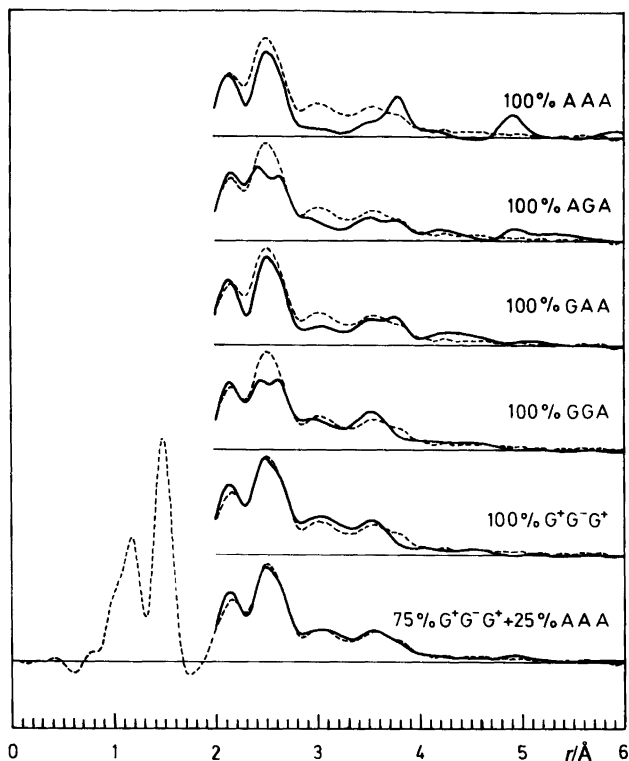
As the preliminary studies strongly indicated that the $G^+G^-G^+$ conformer is the major contributor to the pentynol conformational mixture, this conformer was independently defined by the nec-

Table 2. Calculated vibrational amplitudes (Å) for the C \cdots C and C \cdots O non-bonded distances in five pentynol conformers.

Distance	Conformer ^a				
	AAA	AGA	GAA	GGA	$G^+G^-G^+$
C ² ...O	0.076	0.076	0.076	0.076	0.075
C ⁴ ...O	0.105	0.175	0.183	0.316	0.297
C ³ ...O	0.082	0.178	0.082	0.176	0.176
C ⁵ ...O	0.153	0.193	0.291	0.418	0.409
C ² ...C ⁴	0.085	0.085	0.084	0.084	0.084
C ¹ ...C ³	0.085	0.085	0.085	0.084	0.084
C ³ ...C ⁵	0.052	0.052	0.052	0.052	0.052
C ¹ ...C ⁴	0.085	0.085	0.186	0.185	0.183
C ² ...C ⁵	0.118	0.118	0.118	0.118	0.116
C ¹ ...C ⁵	0.102	0.103	0.270	0.269	0.265

^aThe conformational assignments are described in Table 1.

Fig. 3. Theoretical RD curves ($r > 2.0 \text{ \AA}$) for AA, AG, GA, GG and $G^+G^-G^+$ conformers of pentynol, as well as for 75% $G^+G^-G^+$ + 25% AAA, together with the experimental RD curve.



essary fifteen geometrical parameters. In the beginning of the study the geometries of the other conformers were defined by letting the bond distances be equal to those in the $G^+G^-G^+$ conformer, while the valence and dihedral angles were taken from the MM2 model calculations.

When the mixture of conformers as described above was studied, it proved difficult to get rid of some minor inconsistencies between experimental and theoretical RD curves in the 3.8–4.0 Å

region. This is a region where 1,4 *anti* C...C and C...O distances are expected to appear. Independent CCC and CCO valence angles corresponding to *anti* stereochemistry were therefore introduced, and this clearly improved the agreement between the RD curves in this region.

Several possible models for conformational mixtures of pentynol have been studied, for example those in which:

Table 3. Approximate magnitudes (Å) for the long ($r_{ij} > 2.7 \text{ \AA}$) nonbonded C...C and C...O distances in five pentynol conformers. All conformers have C^2C^5 distances of ca. 3.5–3.6 Å.

Conformer ^a	C ¹ ...C ⁴	C ¹ ...C ⁵	C ³ ...O	C ⁴ ...O	C ⁵ ...O
AA	4.0	5.1	3.8	5.1	6.2
AG	4.0	5.1	2.9	4.3	5.5
GA	3.2	4.1	3.8	4.5	5.4
GG	3.2	4.1	2.9	3.6	4.5
GG ⁻	3.2	4.1	2.9	2.9	3.4

^aThe conformational assignments refer to the C²–C³/C¹–C² dihedral angles.

Table 4. Final results for 4-pentyn-1-ol. Distances in Å, angles in degrees, standard deviations in brackets.

$r(\text{C}\equiv\text{C})$	1.214 (2)	$\angle\text{C}^2\text{C}^1\text{O}^a$	114.9 (1.8)
$r(\text{C}_{sp}-\text{C}_{sp}^3)$	1.461 (2)	$\angle\text{C}-\text{O}-\text{H}$	102 (ass.)
$r(\text{C}_{sp}^3-\text{C}_{sp}^3)$	1.533 (2)	$\angle\text{H}-\text{C}-\text{H}_{Av}$	104.6 (2.0)
$r(\text{C}-\text{O})$	(1.427, ass.)	$\Theta(\text{C}-\text{C}^2-\text{C}^3-\text{C})^a$	73.8 (3.5)
$r(\text{O}-\text{H})$	0.756 (10)	$\Theta(\text{O}-\text{C}^1-\text{C}^2-\text{C})^a$	-71.0 ^d
$r(\text{C}_{sp}^3-\text{H})$	1.089 (2)	$\Theta(\text{H}-\text{O}-\text{C}-\text{C})^a$	70.0 ^d
$r(\text{C}_{sp}-\text{H})$	0.944 (10)	$\angle\text{C}^2\text{C}^3\text{C}^4$ ^b	112.0 (3.0)
$\angle\text{C}^2\text{C}^3\text{C}^4$ ^a	112.9 (1.8)	$\angle\text{C}^1\text{C}^2\text{C}^3$ ^b	111.8 (2.0)
$\angle\text{C}^1\text{C}^2\text{C}^3$ ^a	105.9 (1.6)	$\angle\text{C}^2\text{C}^1\text{O}$ ^b	(112, ass.)
$\alpha(\text{G}^+\text{G}^-\text{G}^+)^c$	0.527 (73)	$R = 0.096$	
Hydrogen bond parameters ($\text{G}^+\text{G}^-\text{G}^+$ conformer):			
$\text{C}^4\cdots\text{H}(\text{O})$	2.27	$\text{C}^4\cdots\text{O}$	2.82
$\text{C}^5\cdots\text{H}(\text{O})$	2.56	$\text{C}^5\cdots\text{O}$	3.19

^aFor the $\text{G}^+\text{G}^-\text{G}^+$ conformer. ^bFor local *anti* stereochemistry. ^cDetermined for the $\text{G}^+\text{G}^-\text{G}^+$ conformer together with MM2-composition (AAA: 9.0 %, AGA: 12.3 %, GAA: 15.6 %, GGA: 10.4 %). Study of the $\text{G}^+\text{G}^-\text{G}^+$ /AAA conformational composition gave $\alpha(\text{G}^+\text{G}^-\text{G}^+) = 0.73(3)$ and $\alpha(\text{AAA}) = 0.27(3)$. ^dDetermined by combined systematic variation/least-squares analysis; see text.

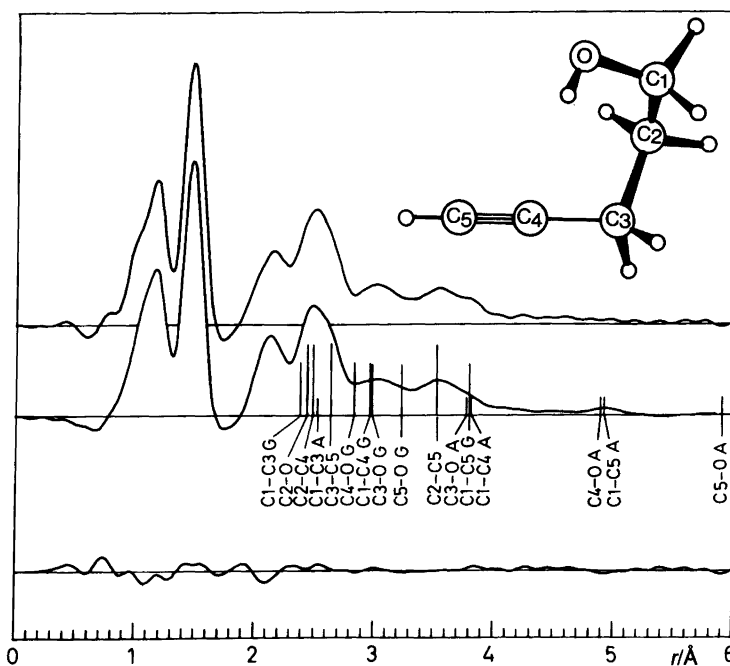


Fig. 4. The experimental RD curve for pentynol together with the theoretical one calculated from the final parameters given in Table 4. The difference curve is also shown.

- (a) the contributions from all five conformers vary freely;
- (b) the $G^+G^-G^+$ and AAA contributions vary freely, while the AGA, GAA and GGA conformers are assumed to be present in equal amounts;
- (c) the $G^+G^-G^+$ and AAA contributions vary freely, there are equal amounts of AGA and GAA conformers, and the contribution from the GGA conformer is fixed at 5%;
- (d) the $G^+G^-G^+$ contribution varies freely, while the relative contributions from the other four conformers are fixed according to their MM2 energies ($G^+G^-G^+$ + MM2-model);
- (e) only $G^+G^-G^+$ and AAA conformers contribute ($G^+G^-G^+$ + AAA-model).

Models a–c had to be rejected because they all resulted in negative conformational contributions. The studies of these models did, however, all indicate that the $G^+G^-G^+$ conformer dominates the conformational mixture and that the AAA conformer contributes substantially.

Models d and e were studied in more detail. Both models resulted in practically identical geometrical parameters, but model d gave the lower *R* factor (0.096 vs. 0.104) and is probably the most realistic of the two. The final results from the study of model d are presented in Table 4, in which the conformational results for model e are also given.

Most of the geometrical parameters were directly determined in the least-squares refinements. Because of high correlation between $r(C_{sp}-C_{sp}3)$ and $r(C-O)$ it was not possible to refine both of them simultaneously, and we chose to fix $r(C-O)$ at 1.427 Å, as determined for 4-penten-1-ol.¹⁵ $\angle C-O-H$, $\Theta(O-C_1-C_2-C)$ and $\Theta(H-O-C-C)$ (for the $G^+G^-G^+$ conformer) were studied indirectly by varying each of them systematically over the expected parameter range. For each fixed parameter value a least-squares analysis was carried out, and the parameter corresponding to minimum *R* factor was chosen for further work. For $\angle C-O-H$ this procedure did not give a clear *R* factor minimum, and this angle was therefore more or less arbitrarily fixed at 102°. The influence of this parameter on the scattering data is, however, negligible.

Fig. 4 shows the theoretical and experimental RD curves. The theoretical curve is calculated

from the geometrical and conformational data given in Table 4. The corresponding experimental and theoretical intensities are shown in Fig. 2.

Infrared measurements

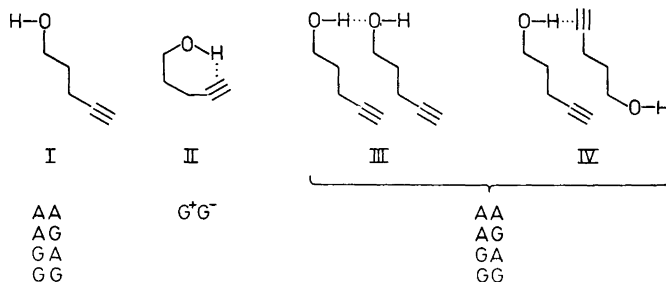
Hydrogen bonding is known to give rise to infrared spectral shift in the O–H stretching region. The IR spectrum of pentynol in CCl_4 solution was studied by Schleyer *et al.*⁶ in 1958. They observed a $\Delta\nu_{O-H}$ shift of 50 cm^{-1} for the hydrogen-bonded conformer. The intensity of the absorption peak was, however, weak. In 4-penten-1-ol a low-frequency O–H stretching band has not been observed with certainty,^{6,15} even though the electron-diffraction study¹⁵ shows that the $OH\cdots\pi$ hydrogen-bonded conformer dominates the conformational mixture. Schleyer⁷ has, however, pointed out that there are many examples of compounds which appear to favour internal $OH\cdots\pi$ interaction, but for which a low-frequency O–H band is missing.

In order to examine the behaviour of n-pentynol we remeasured the infrared spectrum (Fig. 6) of the pure liquid (a), of dilute solutions in CCl_4 (b: 0.1 M, c: 0.01 M) as well as that of the vapour (e: 140°C).

When analysing the spectra of n-pentynol, the fact that four species I, II, III, IV are in equilibrium has to be considered. They differ in their intra- and intermolecular interactions, and this is reflected in the positions of their characteristic group frequencies. The conformers observed by the GED measurements and derived from the force field calculations contribute in various amounts to the four species I to IV, as shown in Scheme 1.

In dilute solution and in the gas phase the characteristic vibrations ν_{OH} , $\nu_{=CH}$, $\nu_{C=C}$ and ν_{C-O} of species I in Scheme 1 should correspond to the frequencies of the uninfluenced monomeric molecules. For species II, III and IV these bands should be shifted to longer wavelengths, and in the case of $OH\cdots OH\cdots OH$ interactions they should additionally be strongly broadened. The bands for II are expected to be rather independent of the concentration, whereas those for III and IV should disappear on increasing dilution, or on change to the gas phase in favour of the bands of I.

As shown in Fig. 6, just this behaviour is ob-



Scheme 1.

served: the spectra display, in fact, three ν_{OH} stretching absorptions: the sharp band at 3650 cm^{-1} is attributed to the molecules of species I; an analogous band of exactly the same frequency is also observed for *n*-pentanol in very dilute CCl_4 solution.

The clearly separated weaker band at 3590 cm^{-1} is attributed to ν_{OH} of species II, because it is observed even in very dilute solution. This assignment is supported unequivocally by the fact that a 0.01 M solution of *n*-pentanol in *n*-pentyne as solvent shows the ν_{OH} frequency of the unassociated molecules exclusively at 3590 cm^{-1} (cf. d in Fig. 6). The third ν_{OH} band appears (Fig. 6: a, b, c) as a broad, diffuse absorption with a maximum at ca. 3500 cm^{-1} ; the band narrows and finally disappears with increasing dilution, or in the gas phase. Additionally, a shoulder on the high wavenumber side of ν_{OH} of the pure liquid (a) at ca. 3550 is attributed to the ν_{OH} of species II because its position corresponds to ν_{OH} of II in dilute solution and this shoulder is missing in the spectrum of undiluted *n*-pentanol. The vapour spectrum of *n*-pentynol (Fig. 6: e) displays the same ν_{OH} bands; as a result of the lack of a solvent effect they are shifted by about 20 cm^{-1} to higher wavenumber.

The stretching vibration (ν_{CH}) of the acetylenic group gives rise to a sharp and strong absorption at 3320 cm^{-1} and a weakly visible shoulder at 3300 cm^{-1} . The ratio of their intensities seems comparable to that for the two ν_{OH} bands of the species I and II. Therefore, we attribute the stronger main $\nu_{\text{C-H}}$ band to $\nu_{\text{=CH}}$ of species I and III, the shoulder originating from the molecules involved in a hydrogen bond between the OH and the acetylenic group (predominantly II and possible IV).

This kind of interaction should influence also the $\text{C}\equiv\text{C}$ stretching frequency $\nu_{\text{C=C}}$. The band is

found as a sharp absorption of medium intensity at 2130 cm^{-1} . Only their reduced steepness on the low-wavenumber side can be taken as an indication that the $\nu_{\text{C=C}}$ absorption is composed of two sub-bands corresponding to the molecules I + III and II + IV, respectively. As an argument in favour of this assignment it may be mentioned that $\nu_{\text{C=C}}$ of *n*-pentyne measured in *n*-pentanol as solvent is found at 2120 cm^{-1} , i.e. 10 cm^{-1} lower than $\nu_{\text{C=C}}$ of *n*-pentyne dissolved in CCl_4 .

By analogy one would also expect the $\nu_{\text{C-O}}$ stretching frequency of *n*-pentynol to be split. Indeed, the broad main $\nu_{\text{C-O}}$ band at 1060 cm^{-1} is accompanied by a separate weaker absorption at 1030 cm^{-1} , which might be assignable to $\nu_{\text{C-O}}$ of pentynol molecules with hydrogen bonds, i.e. II, III, IV. Other vibrations could also contribute to the absorption in this spectral region.

Finally, it is interesting to gain information about the relative concentrations of I, II and (III+IV) that can be obtained from the intensities of the three ν_{OH} bands. A precise analysis would require a decomposition of the overlapping bands to determine their integrated intensity, as well as a knowledge of the extinction coefficients. Without this detailed information the ratio of the concentrations, $C_{\text{I}}:C_{\text{II}}$ can only be estimated to be $\approx 4:1$, derived from the absorbances at the maxima of the sub-bands. This ratio determined from infrared measurements is in qualitative agreement with the data derived from the GED investigation.

Discussion

The present GED study shows that the conformational mixture of gaseous 4-pentyn-1-ol is dominated by the only conformer ($\text{G}^+\text{G}^-\text{G}^+$) having the OH group and the $\text{C}\equiv\text{C}$ bond close enough for intramolecular $\text{OH}\cdots\pi$ attractions to

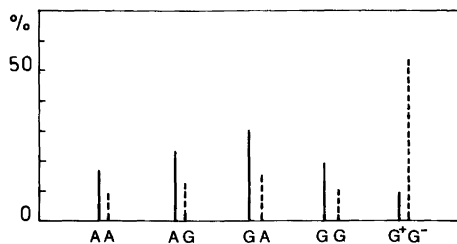


Fig. 5. The conformational composition of pentynol as estimated from the calculated MM2 energies (fully drawn) and the observed conformational composition (stippled).

occur. The study indicates that this conformer constitutes at least 50% of the conformational mixture.

The other conformers (AA, AG, GA, GG) are represented in the final conformational model by relative contributions corresponding to those deduced from their MM2 steric energies (Table 1). The GED data do indicate a substantial contribution from the AA conformer, while the distribution between the other conformers is more uncertain. However, as chemical interest is primarily centered on the $G^+G^-G^+$ conformer, the uncertainty concerning the relative contributions from the other conformers is of minor importance. Nevertheless, it must be remembered that because of the uncertainty about the composition of the non-hydrogen-bonded conformers, the geometrical parameters might be subject to systematic errors.

The present conformational results for 4-pentyn-1-ol complement those recently obtained in a similar study of 4-penten-1-ol.¹⁵ In this latter case the conformational mixture was also found to be dominated by the only conformer having the π system and the OH group in close proximity.

MM2 calculations carried out for simple unstrained hydrocarbons and other simple organic molecules such as alcohols have today reached a level of development where they are generally highly reliable. The MM2 results for such molecules are normally in good agreement with experimental structural results for these compounds.

In the case of 4-penten-1-ol and 4-pentyn-1-ol there are large discrepancies between the calculated conformational compositions, based on the MM2 steric energies, and those deduced from the GED data (Fig. 5). The discrepancies almost cer-

tainly arise because attractive intramolecular $\text{OH}\cdots\pi$ interactions are present that have not been accounted for in the MM2 calculations. In the present case this imperfection of the MM2 program is, however, considered to be an advantage, because an increase in the population of the $G^+G^-G^+$ conformer relative to the calculated (MM2) contribution makes it possible to

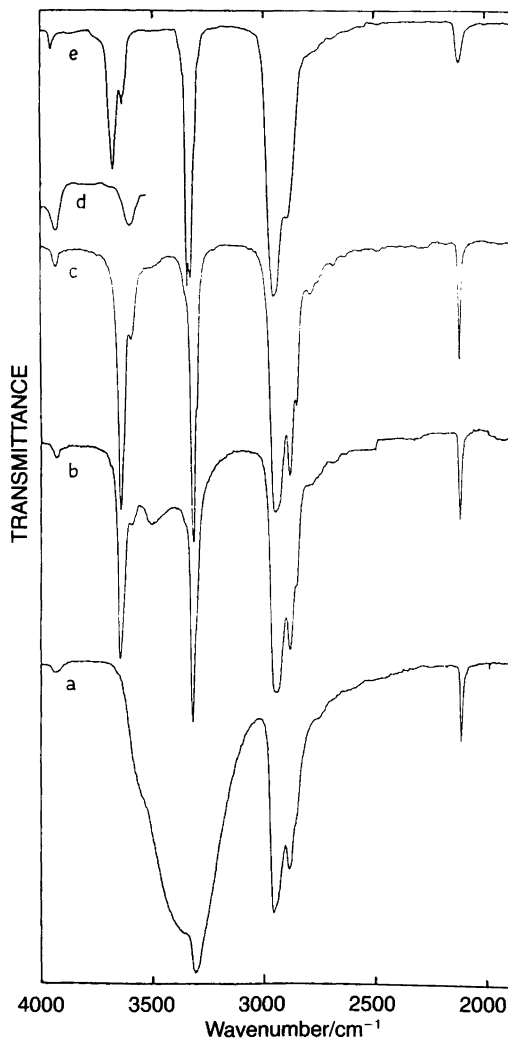


Fig. 6. IR spectra of n-pentanol: (a) pure liquid (capillary film), solution in CCl_4 ; (b) 0.1 M (1 mm); (c) 0.01 M (10 mm all length); (e) vapour 140°C (atmos. pressure; 100 mm all length); (d) solution of n-pentanol in n-pentane (0.01 M, 1 mm all length).

give an estimate of the size of the stabilizing energy due to the $\text{OH}\cdots\pi$ interaction. A 53% contribution from the $\text{G}^+\text{G}^-\text{G}^+$ pentynol conformer, relative to the MM2 estimate of 9.4% (total G^+G^-), corresponds to an extra stabilization of this conformer amounting to ca. 6 kJ mol⁻¹. The stabilization energy due to the $\text{OH}\cdots\pi$ interaction might be larger than this estimate, because the latter represents the total stabilization/steric energy. The CCO and CCC angles of the hydrogen-bonded conformer are for example expected to increase the steric energy of this conformer.

Table 4 gives the distances between the atoms in the hydroxyl group and those in the CC triple bond. The $\text{C}^4\cdots\text{O}$ distance is ca. 0.3 Å and the $\text{C}^4\cdots\text{H}(\text{O})$ distances ca. 0.6 Å smaller than the sum of the respective van der Waals radii.²⁶ This is in accordance with a moderately strong $\text{OH}\cdots\pi$ hydrogen bond.

The observed valence angles of the pentynol $\text{G}^+\text{G}^-\text{G}^+$ conformer are also of interest in the light of the $\text{OH}\cdots\pi$ interactions. $\angle\text{C}^1\text{C}^2\text{C}^3$ is found to be significantly smaller, and $\angle\text{C}^2\text{C}^1\text{O}$ to be larger, than the calculated MM2 angles for this conformer. Both these valence angle changes act to bring the OH group closer to the π system. A decrease in $\angle\text{C}^2\text{C}^3\text{C}^4$ would also have contributed to a reduction in the $\text{OH}\cdots\text{C}\equiv\text{C}$ distance, but is not observed. It is well known, however, that the strength of hydrogen bonding is sensitive to the orientations of the interacting groups. A possible explanation for the valence angle distribution in the pentynol $\text{G}^+\text{G}^-\text{G}^+$ conformer might be that they give the most favourable relative orientation of the OH and $\text{C}\equiv\text{C}$ groups.

The O–H bond length found is unrealistically small. During much of the study, $r(\text{O}–\text{H})$ had been fixed at 0.942 Å, which is a more typical value for this type of bond. The correlation between $r(\text{O}–\text{H})$ and the other geometrical and conformational parameters is, however, negligible. Even if the observed $r(\text{O}–\text{H})$ distance were completely wrong, the inclusion of this variable parameter does not significantly influence the other determined parameters. In the RD curve (Fig. 3) a small peak at ca. 0.8 Å is clearly visible, but as this RD region is often influenced by noise one should not pay too much attention to this observation.

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