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The Conformations of Several Aliphatic Alcohols. The General Occurrence of the Attractive Alkyl/Phenyl Interaction

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The conformation has been studied, by means of NMR spectroscopy, for diastereoisomeric pairs of a series of alcohols having the following general structure:

$$CH_3CH(C_6H_5)CH(OH)\text{-}R$$

where R is a methyl, ethyl, isopropyl, or a *t*-butyl group. It has been demonstrated that the alkyl group (R) is oriented close to the phenyl group in the most preferred conformations; this conclusion is essentially in accord with the results obtained for the structurally related sulfoxides. The general occurrence of an attractive interaction (the CH/π interaction) has, therefore, been suggested between an alkyl and a phenyl group.

In recent years it has become clear that an alkyl group often prefers to be close to a phenyl group in certain molecular environments.[1–3] Thus, in compounds having the general structure of $C_6H_5CH(CH_3)$–X–Bu^t, the *t*-butyl group has been found to orient itself *gauche* to the phenyl group, and *anti* to the methyl group, present in the molecule (Fig. 1). The examples include a sulfide[4] (**1**, X=S), a diastereoisomeric pair of sulfoxides[5,6] (X=SO) and alcohols[2] (X=CHOH), a sulfone[4,7] (X=SO_2), a ketone[8,9] (X=CO), and a hydrocarbon[9] (X=CH_2). Evidence for the hydrocarbon rests on an empirical force-field calculation. The conclusions regarding the other compounds have, in every case, experimental bases (X-ray,[5,7] NMR,[2,5a,8,10] ORD/CD,[5a] dipole moment,[6] IR,[2,9] or product analysis in the stereoselective reactions[1,3,4,11]). We further studied the conformation of a series of diastereoisomeric sulfoxides (**2**), where the *t*-butyl group in the above structure (**1**, X=SO) is replaced by a methyl, ethyl, or isopropyl group.[12] In these cases also, the alkyl group has been shown to be *gauche* to the phenyl group and *anti* to the methyl group in their most preferred conformation (Fig. 2, rotamer **a**). In addition to this, a considerable fraction of the second stable rotamer (rotamer **b**) has been suggested to contribute, whereby the alkyl group is flanked by the phenyl and methyl group; the rotamer **c** seems to be least important.

To account for these findings, an attractive force has been suggested to operate between an alkyl and a phenyl group (CH/π interaction).[1–3] The nature of the weak secondary force remains open, however, we believe this to originate from a hydrogen-bond like interaction of a CH group with the π-system; this might also be regarded as a through-space hyperconjugation. In order to explore the generality of the phenomenon and to obtain insight into the nature of the interactions, the conformation has been studied for diastereoisomeric

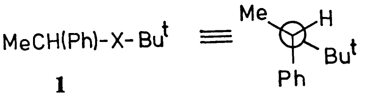

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Fig. 1.

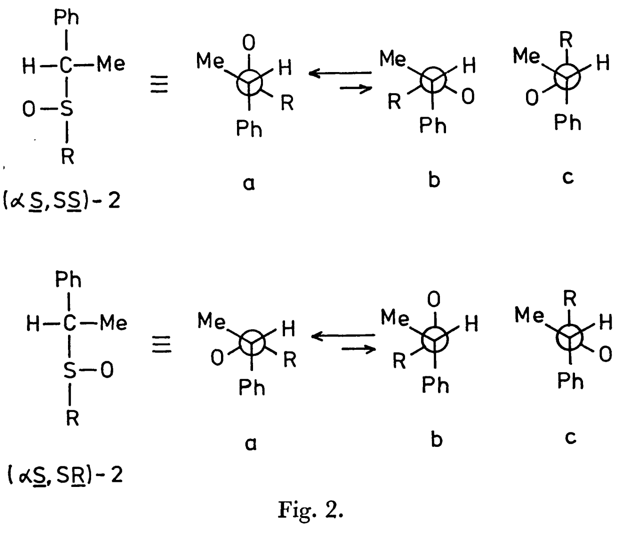
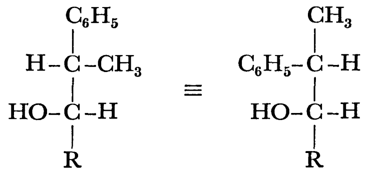


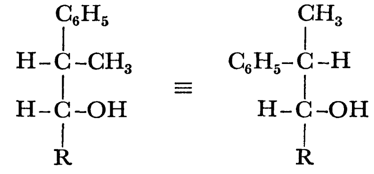
Fig. 2.

(a) *erythro* series



R = CH_3 (2*R*, 3*R*/2*S*, 3*S*: **3**-*er*)
C_2H_5 (2*R*, 3*R*/2*S*, 3*S*: **4**-*er*)
i-C_3H_7 (3*R*, 4*R*/3*S*, 4*S*: **5**-*er*)
t-C_4H_9 (3*R*, 4*S*/3*S*, 4*R*: **6**-*er*)

(b) *threo* series



R = CH_3 (2*R*, 3*S*/2*S*, 3*R*: **3**-*th*)
C_2H_5 (2*R*, 3*S*/2*S*, 3*R*: **4**-*th*)
i-C_3H_7 (3*R*, 4*S*/3*S*, 4*R*: **5**-*th*)
t-C_4H_9 (3*R*, 4*R*/3*S*, 4*S*: **6**-*th*)

Fig. 3.

pairs of a series of alcohols (**3**—**6**), where the sulfoxide function in **2** is replaced by a CHOH group (Fig. 3).

Results

Tables 1 and 2 list the proton and carbon NMR data respectively for the diastereoisomeric pairs of alcohols;

Table 1. Proton NMR parameters[a] for the alcohol diastereoisomers $CH_3CH(C_6H_5)CHOH$-R

	Ar	H_a	Me	H_x	H_y	H_z	OH[b]	J_{ax}[c]
erythro								
3-*er*	7.23	2.63 (2.58)	1.30 (1.22)	3.82 (3.74)	1.07 (0.93)	—	1.82	6.5 (6.7)
4-*er*	7.21	2.75	1.30	3.54	1.39	0.91	1.93	6.5
5-*er*	7.20	2.85	1.28	3.35	1.54	0.88 0.90	1.93	6.5
6-*er*	7.18	2.97	1.27	3.37	—	0.92	2.03	3.7
threo								
3-*th*	7.26	2.66 (2.61)	1.26 (1.22)	3.82 (3.68)	1.19 (1.08)	—	1.57	6.5 (6.3)
4-*th*	7.28	2.74	1.25	3.55	1.54	0.97		6.5
5-*th*	7.30	2.83	1.23	3.39	1.75	0.93 1.01		6.5
6-*th*	7.23	2.98	1.36	3.34	—	0.84		3.9

a) The chemical shifts are reported in ppm downfield from internal TMS ($CDCl_3$). The data in parentheses are those reported in Ref. 14 for CCl_4 solutions. b) The peaks attributed to the OH proton (δ as well as the line shape) are sensitive to the conditions. c) Approximate values; the data are reported in Hz.

Table 2. Carbon NMR parameters for the diastereoisomeric alcohols $CH_3CH(C_6H_5)CH(OH)$-R

	1	2,6	3,5	4	7	8	9	10		11	Δ[a]
erythro series											
3-*er*	144.3	127.8	128.3	126.3	47.2	72.3	16.2			21.0	
4-*er*	144.7	127.7	128.3	126.2	45.4	77.6	27.6	10.4		15.8	
5-*er*	145.2	127.6	128.4	126.1	42.8	81.0	30.1	16.6	20.0	15.8	
6-*er*[b]	148.0	127.4	128.3	125.9	41.1	82.9	36.1	26.8		16.5	
threo series											
3-*th*	143.5	128.0	128.5	126.6	47.9	72.3	17.8			20.5	(+0.5)
4-*th*	143.5	128.1	128.5	126.5	45.6	77.2	27.2	10.0		17.9	(−2.1)
5-*th*	144.0	128.1	128.5	126.5	43.4	80.4	29.9	15.3	20.4	18.6	(−2.8)
6-*th*[b]	144.1	128.8	128.2	126.3	41.7	83.4	35.9	26.7		22.4	(−5.9)

a) Δ=δ(*erythro*)−δ(*threo*). b) Taken from Ref. 2.

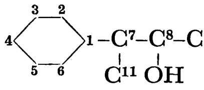


Table 3. The lanthanoid-induced shifts (LIS)[a] for the alcohol diastereoisomers $CH_3CH(C_6H_5)CH(OH)$-R

	Protons							Carbons								
	H_o	H_m	H_a	Me	H_x	H_y	H_z	1	2,6	3,5	4	7	8	9	10	11
erythro series																
3-*er*	0.18	0.07	0.39	0.20	0.61	0.35	—	0.27	0.21	0.11	0.09	0.47	(1.00)	0.49	—	0.27
4-*er*	0.17	0.06	0.39	0.21	0.63	0.38 0.32	0.21	0.27	0.20	0.10	0.09	0.48	(1.00)	0.48	0.28	0.29
5-*er*	0.14	0.06	0.41	0.24	0.64	0.31	0.28 0.20	0.24	0.16	0.10	0.08	0.51	(1.00)	0.48	0.32 0.28	0.34
6-*er*	0.17	0.01	0.35	0.32	0.65	—	0.25	0.25	0.16	0.05	0.04	0.52	(1.00)	0.47	0.28	0.39
threo series																
3-*th*	0.19	0.05	0.34	0.22	0.63	0.35	—	0.30	0.20	0.10	0.08	0.44	(1.00)	0.51	—	0.26
4-*th*	0.22	0.06	0.32	0.25	0.64	0.34	0.16	0.32	0.24	0.11	0.09	0.47	(1.00)	0.48	0.24	0.30
5-*th*	0.25	0.05	0.32	0.26	0.63	0.36	0.17 0.16	0.34	0.25	0.12	0.09	0.50	(1.00)	0.47	0.28 0.21	0.33
6-*th*	0.29	0.06	0.29	0.26	0.65	—	0.18	0.35	0.26	0.13	0.11	0.50	(1.00)	0.43	0.24	0.33

a) The chemical shifts induced by the addition of $Yb(fod)_3$ to $CDCl_3$ solutions. The data are normalized to the value for C(8) carbon (LIS_{rel}=1.00). See Tables 1 and 2 for the numbering of the nuclei.

3-phenyl-2-butanols (**3**), 2-phenyl-3-pentanols (**4**), and 2-methyl-4-phenyl-3-pentanols (**5**). Table 3 lists the lanthanoid-induced shifts (LIS) determined for the proton and carbon resonances. The data for the diastereoisomers of 2,2-dimethyl-4-phenyl-3-pentanol (**6**)[2] are also included for the purpose of comparison. In Figs. 4—6 are reproduced parts of the proton NMR spectra of these alcohols (**3**—**5**).

An inspection of the NMR spectra reveals several interesting features. First, the peaks attributed to the proton α to the hydroxyl group (labeled H_x) are broader in the *threo*[13] alcohols (Figs. 5b and 6b) than in the *erythro* series, and in these cases we did not find any signal appropriate to the hydroxyl proton. Quite a similar result has also been reported for the *t*-butyl homologues (**6**; see Fig. 8 in Ref. 2). The spectrum for a methyl homologue (**3**-*th*; Fig. 4b) is the only exception; here we found a quintet for H_x and a sharp singlet for the hydroxyl proton (sharper than that in **3**-*er*). Second, the peaks assignable to the benzylic proton (H_a) appear, in all cases, as a quintet with an intensity ratio of 1 : 4 : 6 : 4 : 1. This implies that the spin-spin coupling constants between H_x and H_a ($^3J_{H_aH_x}$) are similar to each other among the alcohols examined and that they are not far from the value of 6.5 Hz.[14] This is quite in contrast to the observation for the *t*-butyl homologues (**6**-*er* and **6**-*th*), where $^3J_{HH}$ has been found to be *ca.* 4 Hz in both

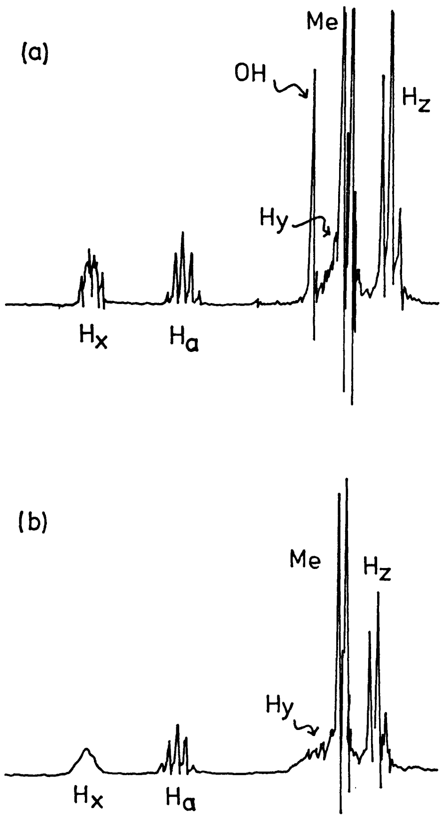


Fig. 5. Proton NMR spectra of (a) **4**-*er* and (b) **4**-*th* obtained for CCl_4 solutions.

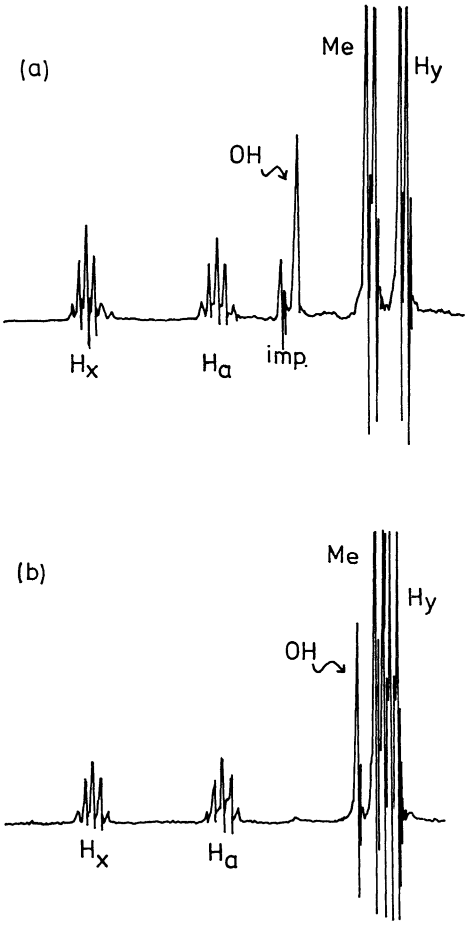


Fig. 4. Proton NMR spectra of (a) **3**-*er* and (b) **3**-*th* obtained for CCl_4 solutions.

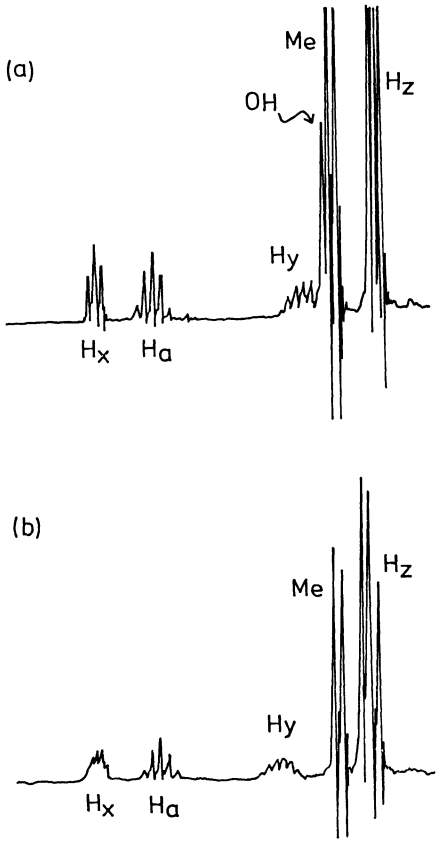


Fig. 6. Proton NMR spectra of (a) **5**-*er* and (b) **5**-*th* obtained for CCl_4 solutions.

cases.[2]

We then carried out the computer-simulation of the LIS[15] for these alcohols; the procedure has been outlined in earlier papers.[2,10,12] The structural parameters were assumed to have the usual values. After several trials and a literature survey, the lanthanoid (Ln)–O–C angle was fixed at 130°.[16,17] The index, A, represents the degree of the distribution of the metal in a mixture of the lanthanoid–substrate complexes (at a given geometry of the substrate) in this equation: $w(\theta)=A/\sqrt{\pi}\ \exp[-A^2\ (\theta-\theta_0)^2]$. On steric grounds, θ_0 was set so that the LSR was always farthest from the phenyl group. A higher value of A, therefore, corresponds to a more localized lanthanoid distribution (centered at θ_0), while the free rotation of Ln in a complex is represented by $A=0$. The Ln–O distance (R) and the torsional angle around the C(7)–C(8) bond were then allowed to vary incrementally at a constant A, in order to search for a reasonable fit of the calculated LIS set [assuming the $(3\cos^2\chi_i-1)/r_i^3$ proportionality] with the observed ones. Figure 7 is a brief illustration of the above procedure; see Ref. 12 for the details.

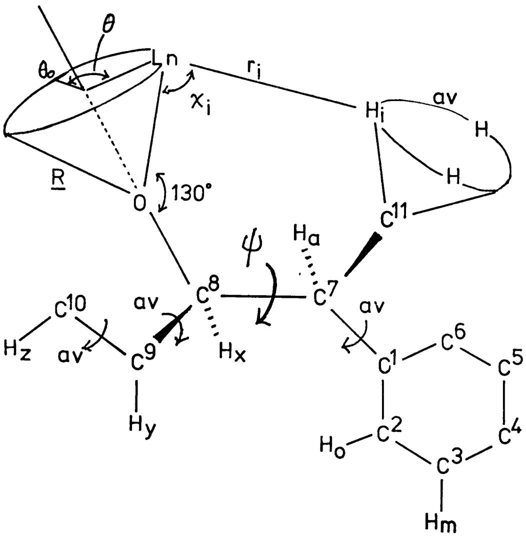


Fig. 7. The procedure for calculating the LIS; av. means the averaging about its rotation (30° increment).

The number of probes which can be used in this program (PSCONT) is limited to 9 nuclei. Therefore, we selected the LIS data which are most appropriate for the present purpose. The data for C(8), which is adjacent to the coordination site, were omitted in view of possible contamination from the contact shift.[18] The data for the β carbons (C7 and C9) should also be used with caution for a similar reason. In order to obtain a reliable result, it is better to use the LIS for the nuclei, the geometrical dispositions of which to the complexation site (OH group) vary with the rotation around the C(7)–C(8) bond. These include the aromatic protons and carbons, H_a, Me, and C(11). Thus, the data which we used for the computation are those for 5—6 protons (H_o and/or H_m; H_a, Me, H_x; H_y and/or H_z) and 3—4 carbons (Cl and/or C2, C3, C4; C9 or C10; and C11). The results have been shown to be rather insensitive to the choice of the probes if an appropriate precaution was taken. The deletion of the carbon LIS, for example, did not significantly affect the qualitative nature of the computed result. The inclusion of the data for C(7), C(8), and/or C(9) did not affect the results appreciably, either, suggesting that the contact shift is unimportant with an ytterbium complex.[18] The Hamilton reliability factor, $AF=[\sum_i(\mathrm{LIS}_i^{\mathrm{obsd}}-\mathrm{LIS}_i^{\mathrm{calcd}})^2/\sum_i(\mathrm{LIS}_i^{\mathrm{obsd}})^2]^{1/2}$, has been used to assess the agreement between the calculated and the observed LIS sets.[19] Figures 8 and 9 plot the AF against the R–C(8)–C(7)–C_6H_5 dihedral angle (ϕ) for these alcohols.[20] The data in Table 4 were extracted from an AF map (R *vs.* ϕ) for a representative case of Compound **5**-*er*.

It should be noted first that, for alcohols having the *erythro* configuration, the essential features of the curve are not significantly affected by a change in the value of A. The minimum AF has invariably been found at ϕ around 60°, accompanied with shallow minima at ϕ *ca.* 160° and 320°. The AF/ϕ profile for the *t*-butyl homologue (**6**-*er*) shows a distinct difference from those of the lower alkyl homologues. Thus, the R/Ph torsional angle at the best agreement is slightly shifted to a larger value ($\phi\approx 80°$), while another, rather profound minimum appears at ϕ *ca.* 135°.

For the *threo* alcohols, **4**-*th*, **5**-*th*, and **6**-*th*, on the other hand, the shape of the profile has been shown to be rather sensitive to the value of A. There is a general tendency for a more reasonable agreement to be found with a higher value of the distribution index; this trend is reasonable on steric grounds.[2,10] In view of this,

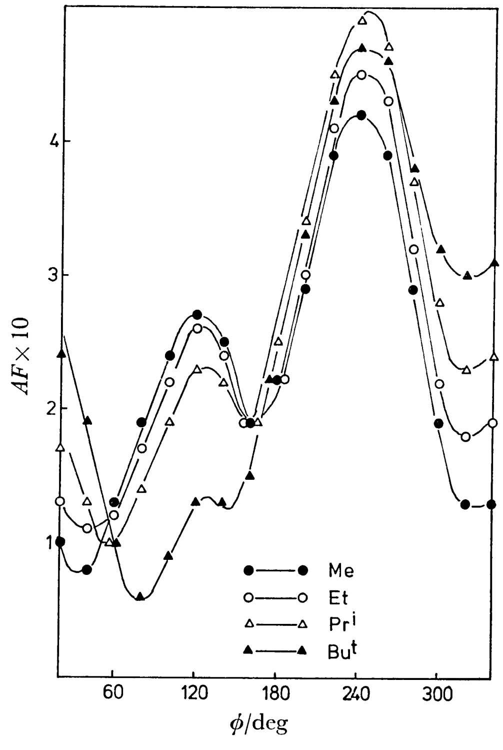


Fig. 8. Plots of AF *vs.* the R/Ph dihedral angle (ϕ) for the *erythro* alcohols, **3**-*er*, **4**-*er*, **5**-*er*, and **6**-*er*. The lanthanoid distribution index (A) and the Ln-O distance (R) are kept constant at 0.8 and 0.30 nm, respectively.

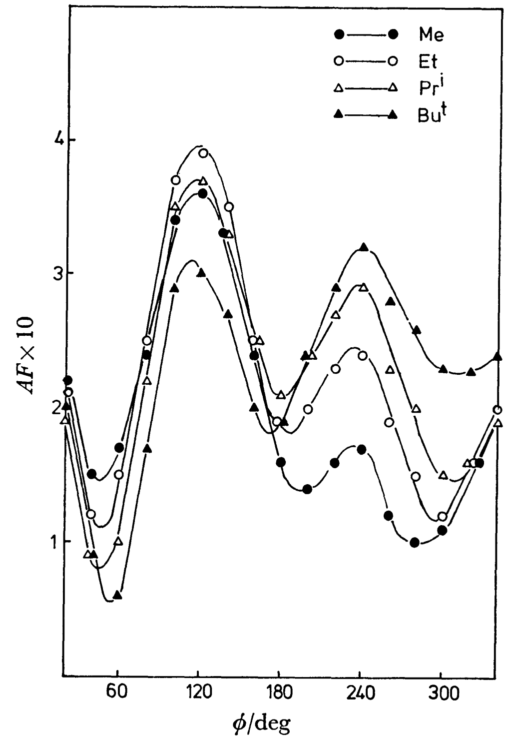


Fig. 9. Plots of AF *vs.* the R/Ph dihedral angle (ϕ) for the *threo* alcohols, **3**-*th*, **4**-*th*, **5**-*th*, and **6**-*th*. The LSR distribution index (A) and the Ln–O distance (R) are kept constant at 0.8 and 0.30 nm, respectively.

Table 4. A part of the AF (in %) maps for **5**-*er* (A=0.8; the monitor nuclei were H_a, Me, H_o, H_m, H_z, H_x, C4, C10, and C11)

	ϕ/deg				
R(nm)	20	40	60	80	100
0.26	45	43	28	21	25
0.28	28	25	18	16	21
0.30	17	13	10	14	19
0.32	11	6	7	12	18
0.34	11	7	8	12	18
0.36	14	12	11	13	19
0.38	17	16	13	14	19

we took the results obtained with a higher value of A as relevant; this is consonant with the experience with the sulfoxide analogues.[12] It is interesting that, in these cases also, the curves are always accompanied by three minima of unequal importance. The best fit has been recorded at ϕ *ca.* 50° for **5**-*th* and **6**-*th*, while the profile of **4**-*th* is accompanied with two minima of *ca.* an equal AF at $\phi \approx 45°$ and 300°. The profile for the methyl homologue (**3**-*th*) represents an exception. The curve is, in essence, insensitive to the change in A, and the best fit has been found at *ca.* 290°.

Discussion

Consideration of the LIS Results. It should be noted at first that the simulated conformations of the molecules represent the weighted-average geometries of the lanthanoid–substrate complex. A possibility remains that the complexation perturbs the rotameric equilibrium of the free substrate. However, for the presently studied alcohols, the vicinal coupling constant, ${}^3J_{H_aH_x}$, remained practically unchanged on the addition of the lanthanoid species. This clearly demonstrates that these molecules are conformationally unperturbed by the coordination.

The computation was carried out on the basis of the assumption that there is an unique contribution from a single conformer. Of course, this is not a correct description of the fact in general, but it represents an approximation. It should be noted that the AF in a profile corresponds to the reliability for the average geometry at a given ϕ and by no means represents the potential energy (or population) of the respective rotamer. A good fit may result, even with this simplest model, if a single, highly preferred rotamer is present in solution. A significant change for the AF would be accompanied, in such a case, with a slight modification in the substrate geometry. However, a geometry corresponding to the minimum AF does not necessarily reflect the most stable one if there are several conformers separated by a low free-energy barrier(s). In such a case, an AF minimum may represent the weighted-average geometry of the possible rotamers. In view of this, it is noteworthy that the AF/ϕ profiles (Figs. 8 and 9) have, in every case, three distinct minima, at ϕ around 60°, 180°, and 300° (*i.e.*, at the staggered geometries of the groups). It is likely that the location of ϕ and the goodness of fit at the respective minimum reflect, though in an indirect manner, the probable geometries of the substrates and the relative importance of the rotamers.

It is suggested that, for all of the alcohols with the *erythro* configuration, the rotamer with $\phi \approx 60°$ (rotamer **a** in Fig. 10) is most populated. In this rotamer, the alkyl group positions itself *gauche* to the phenyl and *anti* to the methyl group. A somewhat twisted conformation ($\phi \approx 80°$) is more plausible for the *t*-butyl homologue. The second stable one is suggested to be the rotamer **c** for **5**-*er* and **6**-*er*, while this is the rotamer **b** in the cases of the lower alkyl homologues (**3**-*er* and **4**-*er*). Note that, in the rotamer **b** the alkyl group is flanked by the methyl and phenyl groups.

In the case of the *threo* alcohols, **5**-*th* and **6**-*th*, the most stable conformation has been suggested to have an R/Ph dihedral angle of *ca.* 60°; the second most stable one seems to be the rotamer **b** for **5**-*th*, but the rotamer **c** for **6**-*th*. The rotamers **a** and **b** can be said to be equally stable for **4**-*th*. The conclusion, in essence, is the same as for the *erythro* alcohols. Thus, the alkyl group, in the preferred conformations, tends to be oriented close to the phenyl group in every case.

The methyl homologue with the *threo* configuration (**3**-*th*) represents an exceptional case. The AF/ϕ profile of this compound suggests that the rotamer **b** is most stable. The rotamers **a** and **c** seem to be relatively unimportant and to have an about equal stability. This trend is different from that of the other alcohols having the same (*threo*) configuration.[21] Consonant with this fact is the observation that the hydroxyl proton in **3**-*th* gives rise to a sharp singlet in the NMR spectrum (*vide supra*). For the *threo* alcohols other than **3**-*th*, the OH peak is absent and the peaks assignable to H_x are broader than those for the *erythro* isomers. The disappearance of the OH proton signal as well as the broadening of the H_x peaks can be ascribed to the presence of the OH/π interaction for the *threo* alcohols.[2,22] Thus, for the *threo* isomers (**4**-*th*, **5**-*th*, and **6**-*th*) where the rotamer **a** (OH/Ph *gauche*) is the most important contributor, the exchange rate of the hydroxyl proton is expected to be slowed down. This likely causes the line broadening (and then disappearance) of the OH signal and the observance of the OH/H_x coupling. For the *erythro* alcohols, on the other hand, the OH group is mostly free from the OH/π complexation (OH/Ph *anti* in the rotamer **a**), thus giving rise to an observable peak. The above exceptional observation for the proton NMR of **3**-*th*, therefore, is in line with the conclusion that the most stable conformer has its OH group *anti* to the phenyl group (rotamer **b**). A question remains, however, as to the reconciliation of the present results with the IR finding[2,22] that the (seemingly) π-bonded OH peak at *ca.* 3595 cm^{-1} is very intense for **3**-*th* relative to those for the other alcohols. It is interesting, at all events, that the findings suggest that the alkyl (methyl) group lies close to the phenyl group in this case also.[23] Figure 10 summarizes the order of stability for the rotamers thus speculated. Note that the relative importance of the rotamers **a** : **b** : **c** varies systematically with a change in the alkyl substituent, R.

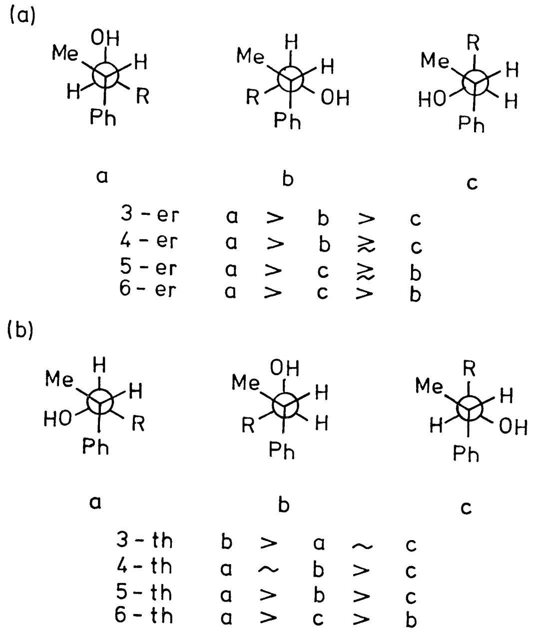


Fig. 10. Possible conformations and the proposed order of the rotamer stability for (a) *erythro* alcohols and (b) *threo* alcohols.

Consideration of the C-13 γ-Effect.[24] The methyl carbon (labeled C11) in **6**-*er* has been shown to be considerably more shielded relative to that in **6**-*th* [$\Delta = \delta(erythro) - \delta(threo) = 16.5 - 22.4 = -5.9$ ppm]. The above phenomenon has been interpreted in terms of the γ-*gauche* effect.[2] In the *erythro* alcohol, the OH group has been shown to be closer to the methyl group (OH/Me dihedral angle *ca.* 40° in the rotamer **a**) than in the *threo* isomer (*ca.* 60°) in their most preferred conformation (see Figs. 8 and 9); thus, the γ-*gauche* effect should be greater for the *erythro* alcohol (**6**-*er*). The result can also be understood in terms of the involvement of a second stable rotamer.[12] For **6**-*th*, the γ-effect (and therefore the shielding) would well be expected to decrease if an appreciable fraction of the rotamer **c** (OH/Me *anti*) is contributing, but this is not so for **6**-*er* (OH/Me *gauche* in the rotamer **c**).

An inverse trend would be expected to be observed for the lower alkyl homologues, for which the relative importance of the rotamer **b** has been suggested. In the rotamer **b**, the OH group is *anti* to Me for the *erythro* alcohols, but is *gauche* to Me for the *threo* isomers. Thus, an involvement of the rotamer **b** would result in the deshielding of the methyl carbon for the *erythro* alcohols, whereas the effect would be not significant for the *threo* alcohols. Therefore, a reversal in the sign of Δ may be observed; this is what we have found for the lower alkyl sulfoxides.[12] This, however, is not the case for the present cases of the ethyl and isopropyl-substituted alcohols. The chemical-shift difference between the isomers (Δ) has, in fact, been found to decrease for the ethyl and isopropyl homologues; however, a reversal in the sign of the shift difference has been recorded only in the case of the methyl homologues (see Table 2). This probably reflects an involvement of the rotamer **c**, but we must reserve further comment until more exact knowledge about the rotameric equilibria becomes available.

Consideration of the Vicinal Spin-Spin Coupling Constants. It has been shown that the spin coupling constant, $^3J_{\mathrm{HaHx}}$, is about 6.5 Hz in all of the alcohols except the *t*-butyl homologues. The foregoing conclusion regarding the rotameric equilibria should be compatible with these data. A simple consideration of the Karplus relationship would require the vicinal coupling constant to be, *e.g.*, *ca.* 11 and 2 Hz respectively[25] for the **a** rotamers of the *erythro* alcohols (H/H *anti*) and of the *threo* ones (H/H *gauche*). A high preference of these conformers, therefore, cannot be an exact description of the fact. The rotamer **a** is, undoubtedly, the most populated one, but the contributions from the other rotamers should also be taken into account. In view of the limitation of the present methodology, only the perfectly staggered rotamers are considered in Fig. 10. As may be perceived by an inspection of the profiles, however, somewhat twisted versions of these conformations must be the real contributors. The above considerations are in line with the results obtained from the LIS-simulation and the C-13 γ-effect.

Possibility of the Attractive Alkyl/π-system Interaction. The importance of the attractive alkyl/phenyl interaction (CH/π interaction) and the consequences thereof have been argued in previous papers.[1–3,26] The suggestion has been made on the basis of some experimental findings and of a MO calculation. We believe that the findings reported here provide strong support for the above suggestion. Thus, in the conformations which are found to be preferred, the alkyl group always orients itself close to the phenyl group, irrespective of the nature of the alkyl group and irrespective of the configuration. We feel further that the OH/π interaction is comparatively unimportant in controlling the conformation of these molecules. The van der Waals (repulsive as well as attractive(27)) and the CH/π interaction seem to be more important in the consideration of these problems.(28) The suggestion that the CH/π interaction may be more important than the OH/π interaction is in line with the HSAB (hard and soft acids and bases) principle(29) that a soft acid prefers to interact with a soft base. Thus, a phenyl group (more generally, a π-system) is a soft base, and the CH hydrogen is softer than OH as an acid. The stabilization energy has been estimated to be very small (*ca.* 3.5 kJ mol^{-1} or less)(1-3) for a single CH/π interaction. In spite of this, we suggest the possibility that the CH/π interaction plays an important role in determining molecular shapes and in controlling the subtle behavior of dynamically interacting systems. Generally, a CH group is present in a structure with some kinds of symmetry (methyl, isopropyl, long-chain alkyl groups, *etc.*). The total stabilization energy would thus become important by an accumulation of multiple CH/π bonds. Further, for obvious reasons, an interaction of this type (CH_3/π as well as CH_3/n; n=lone pair electrons) is entropically advantageous as compared to, *e.g.*, the OH/π interaction. In order to find support for the above suggestion and to ascertain the possible implication, efforts are currently being made in these laboratories.

Experimental

Materials. The alcohols studied in the present work were prepared as has been described in the literature.(14,22) The configurations of these alcohols have been elucidated by Cram,(30) Felkin,(22,31) Kingsbury,(14) and their groups.

NMR Measurements. The proton NMR spectra were recorded on a JEOL MH-100 spectrometer for *ca.* 0.2 M solutions in carbon tetrachloride. The LIS data (^{1}H and ^{13}C) were determined on a JEOL FX-100 instrument for *ca.* 0.2 M solutions in deuteriochloroform, using Yb(fod)$_3$(18) as the LSR. These values were found to be directly proportional to the LSR/substrate ratio up to a value of *ca.* 0.2 eq mol^{-1}.

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