Conformational Equilibria in the 2-Amino-1,2-diphenylethanol System. II. Infrared Studies

Marcus K. Meilahn and Morton E. Munk

Department of Chemistry, Arizona State University, Tempe, Arizona 85281

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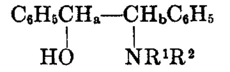
Conformational preferences in a series of 2-(N,N-dialkylamino)-1,2-diphenylethanols (**1a–d**) have been examined by means of high-dilution infrared spectroscopy. With a single exception (**1c**) the *dl-threo* amino alcohols reveal a single, intense absorption band in the 3-μ region, assigned to an intramolecular OH···N bond. In contrast, three absorption bands appear in the spectra of the *dl-erythro* amino alcohols, attributable, in order of decreasing frequency, to the presence of unassociated OH, intramolecular OH···π bonding and intramolecular OH···N bonding. These data are entirely consistent with the assignment of conformational preferences based on nmr, *i.e.*, the conformation of the *dl-threo* amino alcohols (**1c** excepted) may be adequately represented by a single rotamer, tA, and that of the *dl-erythro* amino alcohols by an equilibrium mixture of rotamers, eA and eB.

A conformational analysis of a series of diastereomeric 2-(N,N-dialkylamino)-1,2-diphenylethanols (**1a–d**), employing nmr as a diagnostic tool, has been discussed in a previous paper.[1] That analysis, based on the magnitude of the vicinal coupling constant J_{ab}, attributed an influential role to intramolecular hydrogen bonding with the basic amino group acting as proton acceptor (OH···N).

Infrared spectroscopy provides a powerful and proven tool for the study of hydrogen-bonding phenomena.[2] As such, the method is an alternate route to the examination of conformational preferences in systems in which hydrogen bonding operates.[3] The results of the infrared study reported herein complement the nmr study of the amino alcohols **1a–d**, in part, because of the



$$C_6H_5\underset{\displaystyle HO}{\underset{|}{C}}H_a—\underset{\displaystyle NR^1R^2}{\underset{|}{C}}H_bC_6H_5$$

1a, $R^1R^2 = O(CH_2CH_2-)_2$
b, $R^1R^2 = (CH_2)_5$
c, $R^1R^2 = (CH_2)_4$
d, $R^1 = R^2 = CH_3$

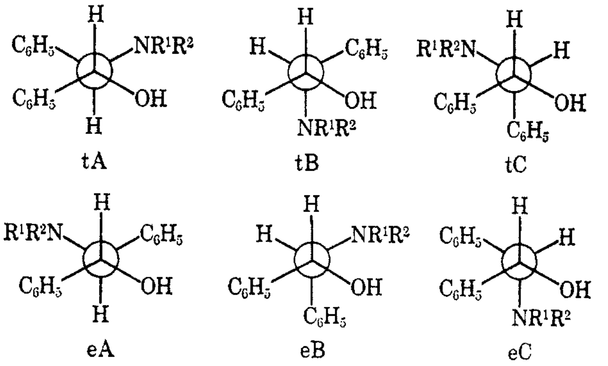
intrinsic differences in the nature of the information derived from the two sources. Briefly, because of the rapid rate of rotation about the central carbon–carbon bond and the difference in the frequency of electromagnetic radiation utilized, an "average" spectrum, weighted to reflect the relative populations of rotamers present at equilibrium, is obtained by nmr, while, in contrast, with infrared measurements it is possible to observe vibrational bands characteristic of each of the rotamers present at equilibrium.

The OH stretching frequencies listed in Table I were determined in a solvent of poor proton-acceptor qualities, carbon tetrachloride, and at high dilution (0.004 *M*) in order to minimize interference by bands characteristic of *intermolecular* hydrogen bonding between amino alcohol molecules. With one exception (**1c**), the spectra of the *threo*[4] amino alcohols **1a–d** reveal only a single, broad absorption band. This intense peak in the 3350–3380-cm^{-1} region is attributed to intramolecularly hydrogen-bonded OH in which the amine nitrogen acts as the proton acceptor (OH···N). Except for the presence of a very weak band ($\epsilon_{OH}/\epsilon_{OH\cdots N} = 0.05$) at 3620 cm^{-1} in the spectrum of the *threo*-pyrrolidino amino alcohol **1c**, *no* absorption characteristic of unassociated OH could be detected in the *threo* series.

Intramolecular hydrogen bonding to nitrogen (OH··· N) would appear to be possible in two of the three rotamers[5] of the *threo* amino alcohols, the *anti* rotamer tA and the *gauche* rotamer tB (Chart I). If a *pure* staggered conformation (*i.e.*, an O–C–C–N dihedral angle of 60°) is assumed, and normal bond lengths and bond angles are employed,[6,7] a N–O distance of 2.85 Å is calculated[8] for rotamers tA and tB. This distance is comparable to the average N–O distance of 2.80 Å observed for the *intermolecular* OH···N bond in the crystalline state.[9] It should be noted, however, that: (a) none of the examples of OH··· N bonding studied in the crystalline state involved an aliphatic hydroxyl and amino group, and (b) the O–H···N angle in the intramolecularly hydrogen-bonded system under study (Dreiding molecular models suggest an O–H···N angle of about 115°) is considerably less than in the examples of intermolecular hydrogen bonding examined, where

Chart I

Rotamers in the *threo* and *erythro* Series



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[1] M. E. Munk, M. K. Meilahn, and P. Franklin, *J. Org. Chem.*, **33**, 3480 (1968).

[2] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

[3] For a review see M. Tichy, *Advan. Org. Chem.*, **5**, 115 (1965).

[4] The terms *threo* and *erythro* as used in this paper indicate *dl-threo* and *dl-erythro*, respectively.

[5] For clarification of the term "rotamer" as used in this paper, see footnote 7, ref 1.

[6] The following bond distances were employed: C–C, 1.54 Å; C–O, 1.43 Å; and C–N, 1.47 Å.[7] Bond angles C–C–O and C–C–N were assumed to be 109.5°.

[7] "Table of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

[8] The problem was reduced to one of calculating the distance between two points in space, whose spherical coordinates are known.

[9] (a) Reference 2, p 289. Values ranging from 2.62 to 2.93 Å are recorded. (b) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, Inc., New York, N. Y., 1968, p 16, also report 2.8 Å as an average observed N–O distance.

TABLE I

INFRARED SPECTRAL PROPERTIES OF AMINO ALCOHOLS[a]

Compound	ν cm^{-1}[b]			$\Delta\nu$ cm^{-1}		$\Delta\nu_{OH\cdots N}$ (*threo*)/ $\Delta\nu_{OH\cdots N}$ (*erythro*)	ϵ			ϵ_{OH}/ $\epsilon_{OH\cdots N}$
	OH	OH···π	OH···N	OH···π	OH···N		OH	OH···π	OH···N	
threo **1a**			3380		240[c]	2.2			34	0
erythro **1a**	3620	3590	3510	30	110		4.9	1.8	17	0.29
threo **1b**			3350		270[c]	2.0			35	0
erythro **1b**	3620	3595	3485	25	135		3.6	3.6	14	0.26
threo **1c**	3620		3360		260	2.4	2.0		36	0.05
erythro **1c**	3620	3575	3510	45	110		1.2	1.1	25	0.05
threo **1d**			3380		240[c,d]	2.4			38	0
erythro **1d**	3620	3590	3520	30	100[d]		2.4	1.2	19	0.13
trans **2**			3460						42	
$C_6H_5CH(OH)CH_2C_6H_5$ (**3**)	3620	3590		30			54	3.0		
$C_6H_5CH(OH)CH_3$ (**4**)	3620						45			

[a] All spectra were determined in carbon tetrachloride solution (0.004 *M*). [b] Probable errors: ±1.5 cm^{-1} for unassociated OH; ±2.5 cm^{-1} for bonded OH band. [c] ν_{OH} = 3620 cm^{-1} is used in calculating $\Delta\nu_{OH\cdots N}$ for the *threo* isomer. [d] Pitha, *et al.*,[13] report $\Delta\nu_{OH\cdots N}$ values of 255 and 110 cm^{-1}, respectively, for the *threo* and *erythro* amino alcohols **1d**.

linearity or near linearity is likely. In connection with the latter point, there is no information presently available that relates the A–H···B angle and the A–B distance.[10]

The absence of unassociated OH absorption in the spectra of the *threo* amino alcohols **1a**, **b**, and **d** indicates that rotamer tC, whose geometry precludes intramolecular OH···N bonding, must be negligibly populated at equilibrium and that the monomeric species exists exclusively as the intramolecularly hydrogen-bonded form. This strong preference for the intramolecularly hydrogen-bonded form is also observed in related systems. *trans*-2-(1-Piperidino)cyclohexanol (**2**) shows no unassociated OH in its high-dilution infrared spectrum; therefore, the monomeric species must reside only in that chair conformation with the two vicinal substituents equatorial to one another and exist exclusively as the intramolecularly hydrogen-bonded form.

It is interesting to note that, whereas neither *cis*- nor *trans*-2-(N,N-dimethylamino)cyclohexanol show unassociated OH absorption in carbon tetrachloride,[11] *cis*- and *trans*-2-amino-[12] and 2-(N-methylamino)cyclohexanol[13] do. Drefahl and Hörhold[14] report the appearance of an unassociated OH band in the high-dilution spectra of *threo*-2-amino- and 2-(N-methylamino)-1,2-diphenylethanol in carbon tetrachloride and carbon disulfide, respectively, but the absence of the same absorption band in the spectrum of *threo*-2-dimethylamino-1,2-diphenylethanol.

Infrared evidence, therefore, would appear to limit the conformational equilibrium in the *threo* amino alcohols **1a**, **b**, and **d** to tA ⇄ tB, but would not define the position of that equilibrium. Nmr studies[1] in chloroform,[15] which indicate the presence of little, if any, of *gauche* rotamer tB or tC at equilibrium, are therefore compatible with and strengthened by this evidence. The strong preference for rotamer tA in the *threo* series has been discussed in steric terms.[1]

The infrared spectrum of the *threo*-pyrrolidino alcohol **1c** is unique to the *threo* series because of the appearance of weak unassociated OH absorption. This unexpected observation, which recalls the anomalies observed in the nmr spectra of pyrrolidino compounds,[1] requires the presence of a detectable amount of one or more of the three rotamers in *unassociated* form. The case for a negligibly populated rotamer tC has been made previously on steric grounds.[1] A comparison of Corey–Pauling–Koltun (CPK) models of rotamer tA of *threo* **1b**[16] and **1c**, in which the groups attached to the ethane backbone are aligned to permit intramolecular hydrogen bonding (OH···N) and minimize steric interaction, reveals greater crowding in the pyrrolidino compound **1c** between the amino group and that phenyl group attached to the same carbon atom, a consequence of the subtle steric requirements unique to the pyrrolidine ring.[17] Because of the favorable orientation of hydroxyl and amino groups for intramolecular hydrogen bonding (OH···N) these differences would not be expected to cause selectively an increase in the population of the unassociated OH form of rotamer tA (designated tA_{OH}) in the case of *threo* **1c**. As previously suggested,[1] however, this congestion in rotamer tA of *threo* **1c** can result in a slight shift of the heavily biased equilibrium tA ⇄ tB to the right. That this shift, *which apparently occurs to any measurable extent only in the case of the pyrrolidino alcohol* **1c**, probably accounts for the appearance of unassociated OH absorption in the spectrum of *threo* **1c** becomes clear from an inspection of CPK models of rotamer tB. With the amino group properly oriented for intramolecular hydrogen bonding, a strained system results due, in particular, to the steric interaction between the amino group and *both* phenyl groups (Figure 1). This crowding in rotamer tB between the amino and the phenyl groups is clearly more severe than in the *anti* rotamer tA and models suggest an alternate orientation of groups, *not conducive* to intramolecular hydrogen bonding (OH···N), which

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(10) Chapter 6 of ref 9b.

(11) K. Adank and W. G. Stoll, *Helv. Chim. Acta*, **42**, 887 (1959).

(12) (a) J. Sicher, M. Horak, and M. Svoboda, *Collect. Czech. Chem. Commun.*, **24**, 950 (1959); (b) G. Drefahl and G. Heublein, *Chem. Ber.*, **94**, 915 (1961).

(13) J. Pitha, M. Horak, J. Kovar, and K. Blaha, *Collect. Czech. Chem. Commun.*, **25**, 2733 (1960).

(14) G. Drefahl and H. Hörhold, *Chem. Ber.*, **94**, 1641 (1961).

(15) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 371 (1963), suggest that chloroform and carbon tetrachloride may be used interchangeably in infrared studies of hydrogen bonding.

(16) The *threo*-piperidino alcohol **1b** serves as the standard of comparison.

(17) Models suggest the focal point of the crowding to be between pseudo-axial hydrogens at positions 2 and 5 of the pyrrolidino group and the carbon atoms of the phenyl group in *threo* **1c** and between the axial hydrogens at positions 2 and 6 of the piperidino group and the carbon atoms of the phenyl group in *threo* **1b**. The particular interaction closely resembles that observed in a comparison of rotamer eA of *erythro* **1d** and **1c** and is illustrated in Figure 1 of ref 1. Although intramolecular hydrogen bonding to nitrogen is precluded in eA, it is interesting to note the similarities in orientation of groups in rotamers tA and eA as suggested by models.

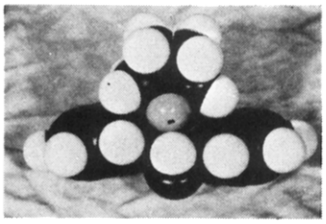

Figure 1.—CPK molecular model of *threo* amino alcohol **1c** as the intramolecularly hydrogen-bonded form of rotamer tB.

minimizes steric crowding. Thus, it may be the presence of rotamer tB in its *unassociated* OH form (tB_{OH}) at equilibrium that accounts for the appearance of weak unassociated OH stretching absorption in the spectrum of *threo* **1c**. It should be noted that the intramolecularly hydrogen-bonded ($OH\cdots N$) form of rotamer tB (designated $tB_{OH\cdots N}$) is strained irrespective of the amino group present, although the strain appears to be greater with the piperidino than with the pyrrolidino group. In retrospect, this slight shift in the equilibrium $tA \rightleftarrows tB$ to the right in the case of *threo* **1c** may be reflected in the slightly lower value of the vicinal coupling constant J_{ab} (by 0.3–0.5 Hz in $CDCl_3$ solution) as compared to those for amino alcohols **1a**, **b** and **d**.[1]

In summary, under the conditions of examination, the conformation of *threo* amino alcohols **1a**, **b**, and **d** may be adequately represented by a single rotamer in its intramolecularly hydrogen-bonded form, $tA_{OH\cdots N}$; that of *threo* **1c** by the equilibrium $tA_{OH\cdots N} \rightleftarrows tB_{OH}$ in which $tA_{OH\cdots N}$ is by far the heavily populated species.

In contrast to the simple spectra observed for the *threo* amino alcohols, the corresponding *erythro* amino alcohols, without exception, display three absorption bands in the 3-μ region (Figure 2). The sharp band at highest frequency is assigned to unassociated OH stretching and appears in each case at 3620 cm^{-1}, a value identical with that observed for the unassociated OH band of 1,2-diphenylethanol (**3**). The band at next lowest frequency, appearing in the range 3575–3595 cm^{-1}, is attributed to an intramolecularly hydrogen bonded OH stretching vibration in which the π-electron cloud of the phenyl ring on the adjacent carbon atom acts as a proton acceptor. The low-frequency and most intense band, appearing in the 3485–3520-cm^{-1} region, is assigned to the OH stretching vibration of the intramolecular $OH\cdots N$ bond. Because of the breadth of the low-frequency band the other two absorption peaks appear as shoulders. For the purpose of measuring frequencies and calculating extinction coefficients in the *erythro* series, the absorption curves are resolved by means of a special-purpose analog computer, the Dupont Model 310 curve resolver.

The absorption band attributed to $OH\cdots\pi$ is assigned on the basis of the known weak intramolecular interaction of hydroxyl groups with suitably disposed π electrons of multiple-bond systems.[3] In this case 1,2-diphenylethanol (**3**) served as a model and its spectrum revealed a barely discernible shoulder on the main absorption band at 3620 cm^{-1} (unassociated OH) which could be identified as a weak band ($\epsilon_{OH}/\epsilon_{OH\cdots\pi} = 18$) at 3590 cm^{-1} after resolution by the curve resolver. The $\Delta\nu_{OH\cdots\pi}$ value of 30 cm^{-1} is comparable to that observed for the *erythro* amino alcohols **1a**–**d**. The absence of such a shoulder in the infrared spectrum of 1-phenylethanol (**4**) suggests that the π-electron interaction indeed involves the phenyl group on the *adjacent* (C-2) rather than on the *same* carbon atom (C-1).

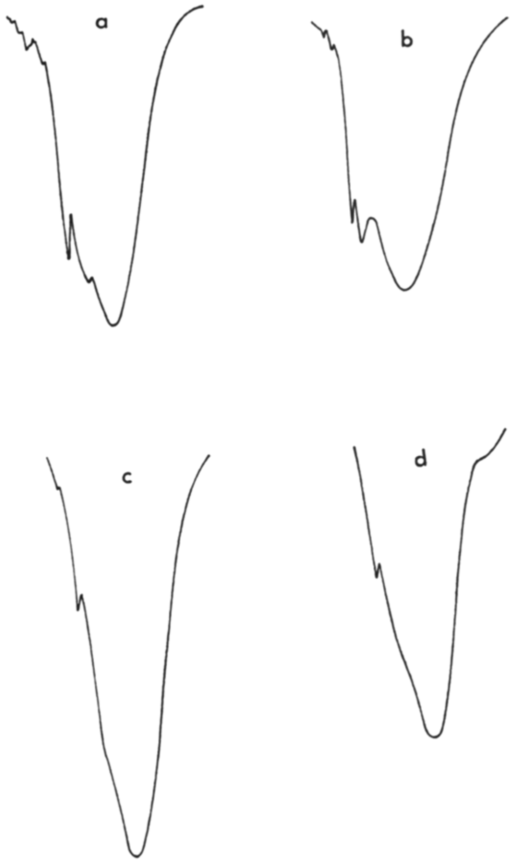

Figure 2.—Infrared absorption spectra of the *erythro* amino alcohols: (a) **1a**, (b) **1b**, (c) **1c**, and (d) **1d**.

In contrast to these findings Drefahl and Hörhold[14] failed to observe the appearance of either unassociated OH or π-bonded OH absorption in the high-dilution infrared spectrum (CCl_4) of the *erythro* amino alcohol **1d**, although absorption characteristic of both of these modes of stretching vibration are observed and assigned by these authors in the spectra of *erythro*-2-amino- (CCl_4) and 2-(N-methylamino)-1,2-diphenylethanol (CS_2); $\Delta\nu_{OH\cdots\pi}$ = 30 and 25 cm^{-1}, respectively. Kanzawa[18] also reports the appearance of a doublet in the 3600-cm^{-1} region ($\Delta\nu = 30$ cm^{-1}) of the spectrum of *erythro*-2-(N-methylamino)-1,2-diphenylethanol, but rejects the operation of such intramolecular hydrogen bonding because of his failure to observe a similar doublet in the spectrum of 1,2-diphenylethanol, a finding in contrast to our own (see above).

The infrared data for the *erythro* amino alcohols **1a**–**d** can be interpreted in terms of conformational preferences if the reasonable assumption is made that rotamer eC is negligibly populated.[19] Intramolecular hydrogen bonding with nitrogen as the proton acceptor is possible then only in *gauche* rotamer eB and, therefore, the intense absorption in the 3485–3520-cm^{-1} region reflects the presence of that rotamer at equilibrium. In the *threo* series it was noted that rotamer tA, with N and O *gauche* to one another, exists exclusively as the intramolecularly hydrogen-bonded form $tA_{OH\cdots N}$. Since

[18] T. Kanzawa, *Bull. Chem. Soc. Japan*, **29**, 604 (1956).

[19] The reasonable assumption is founded on steric factors described in ref 1. In particular, see footnote 10 in that paper.

CPK models of rotamer eB suggest that that orientation of groups required for intramolecular hydrogen bonding to nitrogen minimizes steric crowding as well, it is probable that the same behavior characterizes eB, *i.e.*, rotamer eB exists exclusively as $eB_{OH\cdots N}$.[20] With this as a premise, the appearance of unassociated OH and $OH\cdots\pi$ absorption in the spectra of the *erytho* amino alcohols requires the presence of rotamer eA, a conclusion consistent with nmr data as well.[1] In summary, then, in the *erytho* series the infrared and nmr data are best accommodated by the presence of three species at equilibrium: eA_{OH}, $eA_{OH\cdots\pi}$, and $eB_{OH\cdots N}$.

Molar extinction coefficients and the ratio $\epsilon_{OH}/\epsilon_{OH\cdots N}$ are included in Table I, but only qualitative significance is intended since, in general, hydrogen-bonded OH bands have a higher molar absorptivity than free OH bands.[3] The values of the ratio $\epsilon_{OH}/\epsilon_{OH\cdots N}$ for the *erytho* series, therefore, are compatible with the relative populations of rotamers eA and eB reported on the basis of nmr studies.[1] Noteworthy is the significantly reduced value of $\epsilon_{OH}/\epsilon_{OH\cdots N}$ for the *erytho* amino alcohol **1c** compared to those for *erytho* **1a**, **b**, and **d**. This observation, suggesting that in the *erythro* series the equilibrium eA ⇄ eB lies *farthest* to the right in the case of the pyrrolidino alcohol **1c**, is consistent with the conclusion, deduced from nmr data, that the *least* steric crowding in rotamer eB exists in this compound. Thus, some independent evidence is provided in support of the proposed unique steric requirements of the pyrrolidino group[1] and its conformational implications in sterically encumbered systems.

The foregoing discussion limits intramolecular $OH\cdots N$ bonding to rotamer tA in the *threo* series and rotamer eB in the *erythro* series. It has been suggested that in each case the orientation of nitrogen required for such intramolecular bonding also minimizes steric crowding. In view of this, the striking and consistent differences in $\Delta\nu_{OH\cdots N}$ for the *threo* and *erythro* amino alchols **1a–d** require examination in terms of the proposed conformational analysis since, as pictured in Chart I, the amino and hydroxyl groups are similarly disposed in space in *both* rotamers and, therefore, similar heats of formation (ΔH) and, consequently, similar $\Delta\nu_{OH\cdots N}$ values might be expected in both series.[21] These observed differences lead us to suggest a more detailed description of rotamers tA and eB.

The chemical literature reveals numerous examples of acyclic diastereomeric 1,2-diols and 1,2-amino alcohols in which the $\Delta\nu$ value of the *threo* (or *dl*) compound exceeds that of the corresponding *erythro* (or *meso*) compound.[3] The usually offered explanation,[3] *i.e.*, steric crowding between *gauche* R groups (phenyl groups in the present study) increases the R–C–C–R dihedral angle (*e.g.*, see rotamer tA) and drives A and B closer together in the *threo* (or *dl*) series permitting formation of a stronger $A\text{–}H\cdots B$ bond, is undoubtedly applicable here as well. It is likely that in the system under study an N–O distance somewhat less than the 2.85 Å characteristic of the "pure-staggered" form is optimal.[9] In rotamer tA a $C_6H_5\text{–C–C–}C_6H_5$ angle greater than 60° leads to a decrease in *gauche*-phenyl interaction as well as a decrease in the N–O distance. The result should be an increase in the heat of formation of the $OH\cdots N$ bond, and consequently, the $\Delta\nu_{OH\cdots N}$ value, in the *threo* series. In contrast, in the *erythro* series a $C_6H_5\text{–C–C–}C_6H_5$ angle greater than 60° in rotamer eB leads to an N–O distance greater than 2.85 Å and a concomitant decrease in the heat of formation of the $OH\cdots N$ bond.

That additional factors may be operative in the 2-dialkylamino-1,2-diphenylethanol system is suggested by the surprisingly high $\Delta\nu_{OH\cdots N(threo)}/\Delta\nu_{OH\cdots N(erythro)}$ ratio, 2.0–2.4, as compared to the values 1.2–1.3 reported for diastereomeric acyclic 1,2-diols and other 1,2 amino alcohols.[3] Based on the premise that a decrease in N–O distance from the 2.85 Å of the undistorted, pure-staggered form leads to a strengthening of the $OH\cdots N$ bond, CPK models of rotamer tA and eB were again compared. These models suggest that the previously noted congestion in rotamer tA between the amino group and phenyl on the same carbon atom could result in a decrease of the C–C–N bond angle and, consequently, a decrease in N–O distance. The operation of a similar deformation effect, the Thorpe–Ingold effect, has been suggested to account for the variations observed in $\Delta\nu_{OH\cdots O}$ for a series of 2-substituted propane-1,3-diols.[22] A comparable repulsive interaction leading to deformation of the C–C–N angle does not appear to exist in models of rotamer eB. In effect, then, in the *threo* series a sterically induced decrease in both the O–C–C–N dihedral angle and C–C–N bond angle may reinforce one another and contribute to the larger-than-usual $\Delta\nu_{OH\cdots N}$ values in this sterically encumbered system. This discussion is not intended to imply a thorough understanding of the factors controlling the magnitude of the ratio of $\Delta\nu_{OH\cdots N}$ values, rather, to serve as a point of departure for additional study.

In summary, in the series of 2-dialkylamino-1,2-diphenylethanols examined, infrared evidence confirms the existence of intramolecular hydrogen bonding ($O\text{–}H\cdots N$) and lends support to its importance as a factor in determining conformation. This is most clearly seen in the *erythro* series, where the significant population of *gauche* rotamer eB at equilibrium is the result of a balance between steric control and intramolecular hydrogen bonding.

Experimental Section

Preparation of Compounds.—The *threo* and *erythro* amino alcohols **1a–d** and *trans* **2** were prepared according to the method of Munk and Kim[23] and are described by Munk, Meilahn, and Franklin.[1] Product homogeneity was demonstrated by gas-liquid partition chromatography (6-ft stainless steel column packed with 5% XE-60 on an Anakrom ABS support) prior to high-dilution infrared runs.

1,2-Diphenylethanol (**3**) was prepared by the lithium aluminum hydride reduction of desoxybenzoin, mp 66–67° (Skellysolve B[24]). A commercial sample of 1-phenylethanol (**4**) was carefully distilled prior to the determination of its infrared spectrum.

High-Dilution Infrared Technique.—The infrared spectra of compounds **1–4** were determined at a concentration of 0.004 *M* in carbon tetrachloride (analytical reagent, Mallinckrodt Chem-

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[20] It can be noted that CPK models of rotamers $tA_{OH\cdots N}$, $eB_{OH\cdots N}$, and $tB_{OH\cdots N}$ suggest that rotamer stability decreases in that order. This order, based on an evaluation of the steric environment (crowding) about the amino group, appears to hold for all the amino alcohols examined in this study and parallels the order of rotamer stability reported earlier.[1]

[21] This is in accord with the relationship of R. M. Badger and S. H. Bauer, (ref 2, pp 82–83), since we deal here with a limited series of closely related compounds. See R. West, D. L. Powell, L. S. Whatley, M. K. T. Lee, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

[22] P. von R. Schleyer, *ibid.*, **83**, 1386 (1961).

[23] M. E. Munk and Y. K. Kim, *J. Org. Chem.*, **30**, 3705 (1965).

[24] A petroleum ether fraction supplied by Skelly Oil Co.

ical Works) that had been dried by azeotropic distillation. Matched silica cells (5 cm) were employed and the spectra were recorded on a Beckman Model IR-12 spectrometer in the region 3100–3700 cm^{-1}. The single beam–double beam ratio was adjusted to 1 at a base line of 90% transmittance. The base line was determined with both cells containing the solvent at a scanning speed of 70 cm^{-1}/min. Several milliliters of solvent were then removed by syringe from the sample cell, the alcohol was quickly transferred to the cell, and the solvent was replaced. The cell was stoppered and gently shaken to achieve a homogeneous solution. The spectrum was then recorded at a scanning speed of 70 cm^{-1}/min. All samples were run at room temperature, *i.e.*, 23°. Using identical instrument parameters good reproducibility of spectra was observed.

In the *threo* amino alcohols **1a–d** the peak position of the broad OH···N band could be estimated to an accuracy of about ±2.5 cm^{-1} directly from the spectra. Peak positions of the multicomponent curves (Figure 2) of the *erythro* amino alcohols **1a–d** and 1,2-diphenylethanol (**3**) were assigned after resolution by a special-purpose analog computer, the Du Pont 310 curve resolver. In generating each component of the curve, shapes corresponding to Gaussian distribution were assumed. The positions of the resolved, relatively sharp unassociated OH and OH···π peaks could be estimated to ±1.5 cm^{-1}; the broad OH···N peak was estimated to an accuracy of ±2.5 cm^{-1}. Extinction coefficients were measured by employing peak height. The resolved curve was used to measure peak heights in the case of multicomponent absorption curves.

Registry No.—**1a** (*threo*), 19640-34-7; **1a** (*erythro*), 19640-35-8; **1b** (*threo*), 19640-36-9; **1b** (*erythro*), 19640-37-0; **1c** (*threo*), 19640-38-1; **1c** (*erythro*), 19640-39-2; **1d** (*threo*), 2576-07-0; **1d** (*erythro*), 19640-41-6; **2** (*trans*), 7581-94-4; **3**, 614-29-9; **4**, 98-85-1.

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Alumina-Catalyzed Dehydration of Methylhexadienols. A Reinvestigation[1]

Charles W. Spangler and Nancy Johnson

The Michael Faraday Laboratories, Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

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Catalytic dehydration of substituted hexadienols usually produces a mixture of substituted 1,3,5-hexatrienes and the corresponding substituted 1,3-cyclohexadienes. Alumina dehydration of 1,5-heptadien-4-ol or 3-methyl-1,5-hexadien-3-ol at temperatures ranging from 250 to 350° yielded the expected methyltrienes, but the cyclohexadiene fraction consisted of double-bond isomers whose distribution proved to be temperature dependent. Thermolysis of authentic 1,3,5-heptatriene or 3-methyl-1,3,5-hexatriene over alumina or glass helices yielded similar results. The 1,3-cyclohexadienes formed at 250° can be predicted on the basis of electrocyclic ring closure of an intermediate triene having a *cis* configuration about the central double bond. At 350°, 1,3-cyclohexadiene mixtures, resulting from intramolecular 1,5-hydrogen shifts in the Woodward–Hoffmann product, predominate.

Until very recently, the preparation of substituted 1,3,5-hexatrienes has involved either a vapor phase catalytic dehydration over alumina or an acid-catalyzed dehydration of an appropriately substituted hexadienol. The products isolated from these procedures, in most cases, have been of doubtful purity. Pure substituted 1,3,5-hexatrienes have been prepared by means of a Hofmann elimination.[2–4] It has been established that the major by-product of catalyzed hexadienol dehydration is a corresponding cyclohexadiene. The formation of these cyclohexadienes has been described by Woods and coworkers,[5,6] who considered thermal trienic ring closure an internal Diels–Alder reaction. However, Woodward and Hoffmann[7] now describe it as a disrotatory electrocyclic transformation.

Woods and Fleishacker[5] attempted the preparation of the three possible methyl-1,3,5-hexatrienes by dehydration of appropriately substituted hexadienols over alumina, however, only 1,3,5-heptatriene was obtained in a relatively pure state. The 2-methyl- and 3-methyl-1,3,5-hexatrienes were apparently contaminated with appreciable quantities of methylcyclohexadienes. These workers also reported that either dehydration of the methylhexadienol over alumina at 500° or passage of methyl-1,3,5-hexatriene over the catalyst under the same conditions yielded methylcyclohexadienes of indeterminate double-bond position. We have recently shown[8] that under the experimental conditions employed by Woods and Fleischacker, cyclization followed by dehydrogenation to toluene is also an important reaction. Hence, it is probable that products formed at these temperatures were contaminated with toluene.

Lewis and Steiner[9] have studied the cyclization of 1,3,5-hexatriene and found that the purely thermal cyclization of the *cis* isomer was practically quantitative at 120–190°; the *trans* isomer was unaffected. We decided, therefore, to reinvestigate both the catalytic dehydration of methylhexadienols and the thermal cyclization of the pure methyl-1,3,5-hexatrienes at temperatures lower than those employed by Woods, *et al.*, in order to suppress the methylcyclohexadiene to toluene reaction. We also hoped to elucidate the structures of the methyl cyclohexadienes formed in both of the above reactions.

Both 1,5-heptadien-4-ol (**1**) and 3-methyl-1,5-hexadien-3-ol (**2**) were dehydrated in the vapor phase over activated alumina at 250° and at 350°. Table I summarizes the products obtained from these dehydrations.

Application of earlier[5–9] observations on dienol dehydration to the alumina-catalyzed dehydration of either **1** or **2** would lead one to predict the reaction sequences given in Scheme I. Although most previous

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[2] C. W. Spangler and G. F. Woods, *J. Org. Chem.*, **28**, 2245 (1963).

[3] C. W. Spangler and G. F. Woods, *ibid.*, **30**, 2218 (1965).

[4] J. C. H. Hwa, P. L. de Benneville, and H. J. Sims, *J. Amer. Chem. Soc.*, **82**, 2537 (1960).

[5] H. Fleischacker and G. F. Woods, *ibid.*, **78**, 3436 (1956).

[6] G. F. Woods and A. Viola, *ibid.*, **78**, 4380 (1956).

[7] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

[8] C. W. Spangler, *J. Org. Chem.*, **31**, 346 (1966).

[9] K. E. Lewis and H. Steiner, *J. Chem. Soc.*, 3080 (1964).