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Role of Secondary Interactions in the Conformational Equilibrium of 2,6-Diisopropylphenol

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The experimental infrared spectrum of 2,6-diisopropylphenol in dilute CCl_4 solution displaying absorptions at 3619 (intense) and 3641 cm^{-1} (shoulder) in the O−H stretching region cannot be satisfactorily reproduced by two symmetric band components. Ab initio quantum chemical calculations have identified *five* stable conformers differing in the relative orientations of the two ortho substituents, whereas DFT calculations yielded *four* different νOH frequencies for these conformers in agreement with the deconvolution and least-squares curve analysis of the experimental spectrum. The observed spectrum could be successfully simulated by the calculated frequencies and band intensities assigned to the five conformers on the basis of their relative stabilities.

Introduction

The frequency of the O−H stretching vibration in phenols is known to be sensitive to the environment. Apart from the spectacular changes in frequencies, band intensities, and bandwidths caused by hydrogen bonding, the frequency shifts of the νO−H band of essentially free OH groups brought about by variation in the electron donating/attracting power of the substituents on the ring are on the order of 10−20 cm^{-1}. Data also indicate that certain bulkier substituents in ortho position to the OH group influence the O−H stretching frequency through secondary interactions between nonbonded atoms.

Thus, the absorption band of the O−H stretching fundamental vibration in CCl_4 solution appears around 3620 cm^{-1} in the IR spectra of phenols having ortho positions substituted by methyl, ethyl, or isopropyl groups,[1] while the corresponding band is found at 3648 cm^{-1} in the case of 2,6-ditertiarybutylphenol.[1,2] Both bands of higher and lower frequencies are present in the spectrum of 2-tertiarybutylphenol.[1] Since the O−H bond is coplanar with the aromatic ring,[3,4] two stable conformers are available for the latter compound: cis (the O−H points toward the substituent) and trans (the O−H points away from the substituent), corresponding to the higher and lower frequency, respectively.[1,5]

At first sight, the spectrum of 2,6-diisopropylphenol displays two νO−H bands: a stronger one with its peak at 3619 cm^{-1} and a well-separated shoulder[2,6] around 3641 cm^{-1}. By analogy, the higher frequency component has been tentatively assigned[6] to a particular conformer in which the OH group points between two methyl groups of the 2-isopropyl substituent, while the lower frequency band of higher intensity has been tentatively assigned to sterically favored conformers obtained by turning the 2-isopropyl group such that the OH group is in an environment resembling a 2-ethyl substitution. At this stage the conformation of the other isopropyl group (the one behind the O−H bond) was thought to be insignificant.

However, as the experimental IR spectrum of 2,6-diisopropylphenol could not be satisfactorily reproduced by two calculated absorption band components, we decided to investigate the possible role of conformation of the 6-isopropyl group that is behind the phenolic O−H bond.

Methods

Infrared spectra of CCl_4 solutions of 2,6-diisopropylphenol were recorded with a Nicolet Magna 750 FTIR spectrometer at 1 cm^{-1} resolution in the concentration range from 2.54×10^{-4} to 2.16×10^{-1} mol/L using KBr and NaCl liquid cells of path lengths ranging from 10 cm to 0.125 mm. No sign of self-association of 2,6-diisopropylphenol was observed up to 3×10^{-2} mol/L.

Decomposition of overlapping band components in the measured IR spectra was done by a least-squares curve analysis program PCCAP developed in our laboratory.[7] The best fit was achieved when approximating the individual components by Gauss−Cauchy product functions.

Calculations of molecular mechanics (MM) have been performed by the Sybyl 6.6 program (Tripos Inc., St. Louis, MO) on a Silicon Graphics Octane workstation under the Irix 6.5 operation system. The MM calculations were based on the MMFF94 force field,[8] applying energy minimization by the conjugate gradient technique with 0.001 kcal/mol Å gradient. Conformer geometries obtained by the MM method were optimized with the Gaussian-94 program[9] at the ab initio RHF level, applying the 6-31G** basis set and very tight convergence criteria. It has been tested that the configurations found are true minima (no imaginary frequencies). (All computations related to vacuum.) In a follow-up calculation by a preliminary version of the APOST program,[10] the molecular energy was dissected to atomic and diatomic components[11] in order to interpret secondary interactions operative within the molecule. For these calculations, we used a very early version of the APOST program,[10] and therefore we were forced to restrict the calculations to the 4-31G level. However, this has no significant effect on the relative magnitude of different quantities.

Full geometry optimizations followed by force field and vibrational frequency calculations were performed for all stable conformers by the density functional (DFT) method as well,

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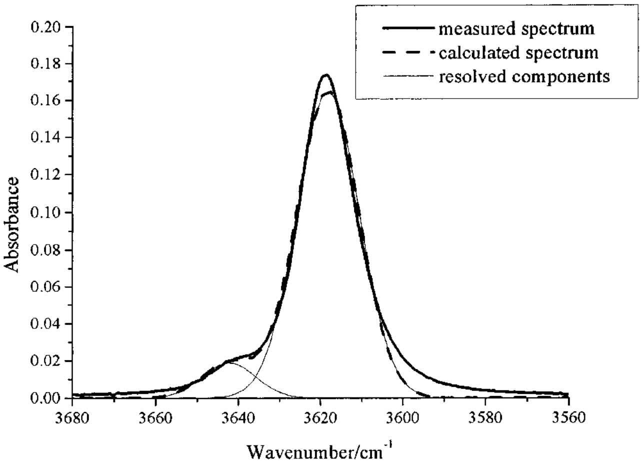

Figure 1. Infrared absorption spectrum of 2,6-diisopropylphenol in dilute CCl_4 solution (3.7×10^{-3} mol/L) in the 3560−3680 cm^{-1} region (solid line), and the result of least-squares fitting of the spectral curve by only two components (broken line).

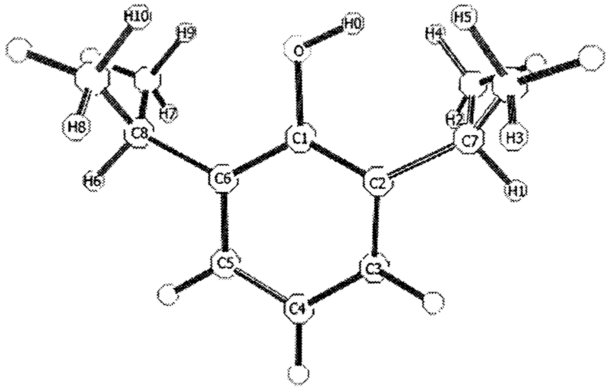

Figure 2. Numbering of atoms and definition of torsion angles describing the conformation of 2,6-diisopropylphenol (τ_1: C5−C6−C8−H6, τ_2: C3−C2−C7−H1, τ_3: C2−C1−O−H0, ω: C2−C1−O).

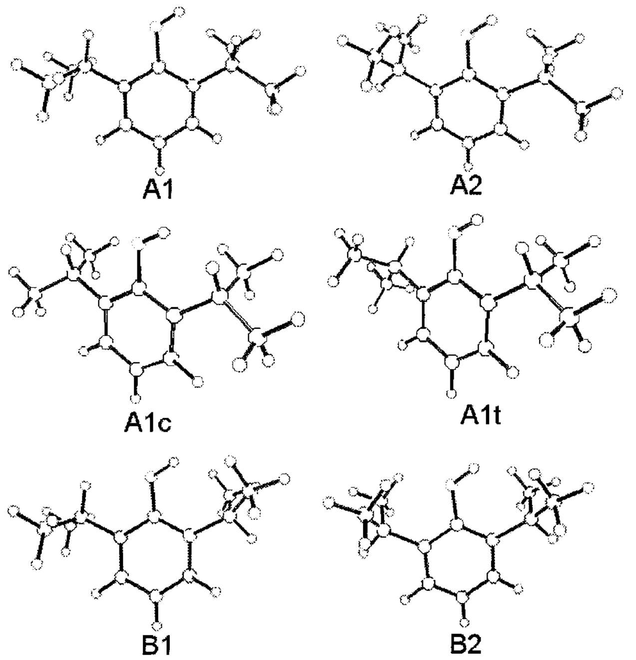

Figure 3. Stable conformers of 2,6-diisopropylphenol optimized by MMFF94 and ab initio RHF/6-31G** calculations (for the values of torsion angles defining these structures, see Table 1).

applying the B3LYP functional and standard 6-31G* basis sets. These calculations were done by means of the Gaussian-94 suit of programs[9] run on a Silicon Graphics Origin 200 computer.

Results and Discussion

A typical infrared spectrum of 2,6-diisopropylphenol in the 3560−3680 cm^{-1} region as observed in a 3.7×10^{-3} mol/L CCl_4 solution is given in Figure 1. This figure also shows the result of decomposition of the spectral curve by only two components; it is evident that the agreement between the measured and calculated curves is less than satisfactory ($r^2 = 0.9873$). Because of this, calculations were performed to identify further conformers by taking into account the rotation of *both* isopropyl groups. The numbering of atoms and definition of the torsion angles are given in Figure 2.

The MM calculations performed in order to find minimum energy conformations were done by varying τ_1 between 0° and 360° in 10° steps and by keeping τ_3 at 0°. The energy was minimized and the energy profile constructed. Energy minima were found at $\tau_1 = 0°$ and $\tau_1 = 180°$ with an energy barrier of 6.5 kcal/mol between them. Similar calculations for the τ_2 torsion angle yielded $\tau_2 = 0°$ and $\tau_2 = \pm 140°$ with an energy barrier as high as 10 kcal/mol at $\tau_2 = 80°$. The stable conformers found (**A1**, **A2**, **B1**, and **B2**, see Figure 3), were further optimized by ab initio calculations at the RHF/6-31G** level and by DFT (B3LYP/6-31G*) calculations. The resulting energies and some relevant geometric parameters and nonbonded interatomic distances are listed in Table 1. It should be noted that the torsion angles obtained by molecular mechanics (except for conformer **A1**) are in good agreement with the ab initio and DFT optimized values. For the **A1** conformer, in which H6 was found to be in the plane of the ring by MM calculations, ab initio and DFT yielded $\tau_1 = \pm 38°$ and $\tau_1 = \pm 40°$, respectively; in other words, conformer **A1** can adopt either cis (**A1c**) or trans (**A1t**) conformation by evidence of quantum chemical calculations (cf. Figure 3). An important finding is the insignificant energy difference of **A1c** and **A1t**; it indicates that stereostructure of these conformers do not influence the interaction of isopropyl and OH groups.

Several distances between nonbonded atoms are found to be less than 2.5 Å, indicating possibly strong secondary interactions between these atoms. Thus, it may be expected that rotation of the isopropyl groups influences the strength and the stretching frequency of the O−H bond.

Owing to the repulsion between the phenolic hydrogen and the hydrogen atoms of the 2-isopropyl group, angle ω (C2−C1−O) is always greater than 120°. The energy of conformers labeled **1** (i.e., **A1c**, **A1t**, and **B1**) is somewhat lower than that of the respective conformers labeled **2**. On the other hand, the influence of rotation of the 2-isopropyl group on the energy is greater: the OH repulsion is smaller in conformers **A**, so they are more stable than conformers **B**. This gives justification to the early suggestion on steric interaction of OH and isopropyl groups.[6]

To characterize the secondary interactions operative in the molecule, the energy was analyzed by the energy decomposition method.[11] The results are collected in Table 2. All nonbonded H···O interactions are of attractive character, the strongest of which represents 6% of the energy of the O−H covalent bond, a finding worth to be noted. While the H6···O attraction is the strongest of all nonbonded interactions in conformers **A1c**, **A1t**, and **B1**, the sum of slightly smaller interaction energies of H9···O and H10···O in conformers **A2** and **B2** exceeds the former.

The O−H fundamental stretching frequencies of the five

TABLE 1: Ab Initio (RHF/6-31G) and DFT (B3LYP/6-31G*) Calculated Energies and Selected Geometric Parameters of the Five Stable Conformers of 2,6-Diisopropylphenol**

	E (hartree)	τ_1 (deg)	τ_2 (deg)	ω (deg)	nonbonded interatomic distances (Å)									
					H0···H1	H0···H2	H0···H3	H0···H4	H0···H5	O···H6	O···H7	O···H8	O···H9	O···H10
					RHF/6-31G**									
A1c	−539.7963	−146.6	141.9	121.6	1.89	2.40	4.17	3.72	4.59	2.38	4.43	2.74	4.86	3.99
A1t	−539.7963	145.8	142.3	121.7	1.90	2.37	4.18	3.70	4.58	2.37	2.74	4.42	3.99	4.86
A2	−539.7958	0.0	±142.0	121.3	1.88	2.39	4.16	3.71	4.58	3.88	3.56	3.58	2.48	2.49
B1	−539.7943	180.0	0.0	121.9	3.58	3.28	3.28	2.00	2.00	2.26	3.73	3.73	4.63	4.63
B2	−539.7942	0.0	0.0	121.8	3.58	3.28	3.28	2.00	2.00	3.88	3.57	3.57	2.48	2.48
					(B3LYP/6-31G*)									
A1c	−543.3504	−142.3	139.6	121.7	1.88	2.27	4.22	3.63	4.56	2.40	4.47	2.69	4.78	4.00
A1t	−543.3504	143.0	139.6	121.7	1.88	2.27	4.20	3.63	4.56	2.40	2.71	4.46	3.92	4.77
A2	−543.3502	0.0	±139.5	121.2	1.87	2.26	4.18	3.62	4.55	3.91	3.60	3.60	2.47	2.47
B1	−543.3490	180.0	0.0	122.1	3.57	3.28	3.28	1.95	1.95	2.26	3.74	3.74	4.65	4.65
B2	−543.3490	0.0	0.0	121.7	3.55	3.25	3.25	1.94	1.94	3.91	3.60	3.60	2.47	2.47

TABLE 2: Diatomic Contributions to the Total RHF 4-31G Energy (in Hartree) in Stable Conformers Obtained at the RHF/6-31G Level**[a]

conformers	O···H6	O···H7	O···H8	O···H9	O···H10
A1c	−0.0408	−0.0149	−0.0320	−0.0125	−0.0152
A1t	−0.0408	−0.0320	−0.0149	−0.0152	−0.0125
B1	−0.0469	−0.0184	−0.0184	−0.0129	−0.0129
A2	−0.0176	−0.0174	−0.0174	−0.0390	−0.0390
B2	−0.0176	−0.0174	−0.0174	−0.0390	−0.0390

[a] For comparison: the contribution of the O−H covalent bond is −0.7084 hartree.

TABLE 3: Comparison of Four Calculated (DFT/B3LYP/6-31G*) and Measured (Resolved) O−H Stretching Frequencies Assigned to the Five Stable Conformers of 2,6-Diisopropylphenol

νOH (cm^{-1})	**A1c, A1t**	**A2**	**B1**	**B2**
calculated (raw)	3776	3773	3814	3811
calculated (scaled)[a]	3612	3609	3648	3645
measured (resolved)	3619	3613	3643	3640

[a] Obtained by multiplying all calculated frequencies by 0.9565.

conformers calculated by the DFT method are given in Table 3. The raw (unscaled) values are listed in the first row, while the second row of Table 3 contains the wavenumber values scaled by a factor of 0.9565 for all five conformers for better agreement with the experimental data. This scaling of the OH stretching frequency corresponds to a scaling of the O−H stretching force constant by 0.915 which is in good agreement with the recommended scale factor (0.920) for such a bond in density functional derived force field calculations[11] at the B3LYP/6-31G* level. The calculated frequencies depend on the internal rotation of *both* isopropyl groups, indeed. A larger shift of frequencies is due to the rotation of the 2-isopropyl group (~30 cm^{-1}). The frequency is lower for conformers **A** representing an "ethyl-like" environment for the O−H bond, while the higher frequencies correspond to conformers **B** trapping the O−H bond between two methyl groups, thus resembling a tertiary butyl substitution. The influence of the 6-isopropyl group on the νO−H frequency through C−H···O secondary interactions is smaller; the curve resolution predicts a shift of 6 cm^{-1} for the lower and 3 cm^{-1} for the higher frequencies. The result of calculations shows a shift of 3 cm^{-1} for the difference between **B1** and **B2** in accord with the deconvolution result. No considerable difference was found between the streching frequencies of **A1c** and **A1t** conformers in agreement with their identical energies; their frequency differs by the same 3 cm^{-1} from that of **A2**. Since **A1c** and **A1t** have the same frequency, we are dealing with four different νO−H frequencies only, as found by the curve resolution. Of the 6-isopropyl rotamers, those labeled **2** are associated with the lower frequencies, because the sum of secondary interactions with two methyl hydrogens weaken the O−H bond more than does a larger but single interaction with the tertiary hydrogen atom in rotamers **1** (cf. Table 2).

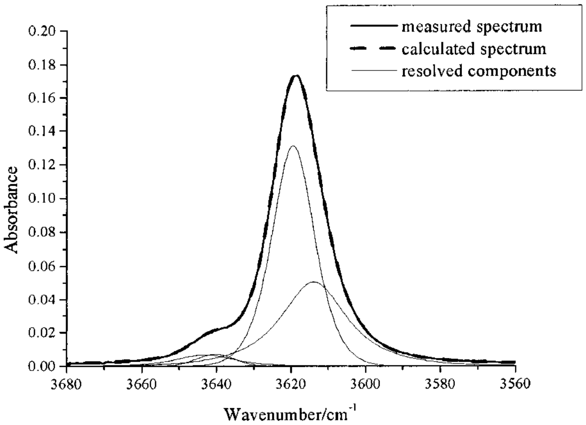

Figure 4. Result of least-squares fitting (broken line) of the O−H stretching region (the same spectral curve as in Figure 1, solid line) by four symmetric band components.

Finally, the reconstruction of the experimental spectrum by four symmetric band components corresponding to the rotamers give an excellent fit ($r^2 = 0.9999$), as shown in Figure 4. In addition to the good agreement between the observed and calculated frequencies (and frequency shifts), there is also a satisfying correlation between the observed (resolved) band intensities and calculated conformer energies: the low energy conformers **A1c**, **A1t**, and **A2** give rise to the two intense νO−H band components, while the energetically less favored conformers are associated with the much weaker, higher frequency absorptions.

Conclusion

Five conformers of 2,6-diisopropylphenol representing isopropyl rotamers contribute to the pattern of IR absorption in the region of O−H stretching frequencies. The rotamers represent energy minima stabilized by intramolecular secondary interactions strong enough to influence the strength of the O−H bond. It has been established that the shoulder at 3641 cm^{-1} is due to energetically less favored conformers **B** of the 2-isopropyl group, while the asymmetry of the intense absorption around 3620 cm^{-1} is the consequence of different influences of 6-isopropyl rotamers.

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References and Notes

(1) Ingold, K. U.; Taylor, D. R. *Can. J. Chem.* **1961**, *39*, 471.

(2) Bellamy L. J.; Williams R. L. *Proc. R. Soc.* **1960**, *A254*, 119.

(3) Hehre, W. J.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1972,** *94*, 1496.

(4) Ingold, K. U. *Can. J. Chem.* **1960**, *38*, 1092.

(5) Simonyi, M.; Kovács, I.; Kardos, J.; Holly, S. *Spectrochim. Acta* **1976**, *32A*, 1387.

(6) Simonyi, M.; Kovács, I.; Kardos, J.; Holly, S. *Tetrahedron Lett.* **1975**, *19*, 1631.

(7) Varga, J.; Lejtovicz, J. *PCCAP Curve Analysis Program*; CRIC: Budapest, 1991.

(8) Halgren, T. *J. Am. Chem. Soc.* **1990,** *112*, 4710.

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision B.3*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(10) Mayer, I.; Hamza, A. Program “APOST”, Version 1.0 (Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences), Budapest, April 2000. (It can be downloaded from the Internet at the following addresses: ftp://kvk.chemres.hu and http://occam.chemres.hu/programs).

(11) Mayer, I. *Chem. Phys. Lett.* **2000**, *332*, 381. Mayer, I.; Hamza, A. *Theor. Chem. Acc.* Accepted for publication.

(12) Rauhut, G.; Pulay, P. *J. Phys. Chem.* **1995,** *99*, 3093.