Tetrahedron Letters No.15, pp. 1587-1590, 1966. Pergamon Press Ltd.
Printed in Great Britain.

ENERGETICS OF THE INTRAMOLECULAR OH...π INTERACTION IN 2-PHENYLETHANOL*

P.J. Krueger and H.D. Mettee

Department of Chemistry, University of Alberta,

Calgary, Alberta, Canada

(Received 2 December 1965; in revised form 12 February 1966)

Although the existence of intramolecular OH...π hydrogen bonds has been well established by spectroscopic measurements (1-5), relatively little work has been done on the energy of this interaction. The infrared absorption spectrum of 2-phenylethanol in dilute CCl_4 solution exhibits two fairly well resolved absorption bands in the fundamental OH stretching region (Fig. 1(a)). The high frequency component at $3635._4$ cm^{-1} can be assigned to "free" OH groups (groups not involved in intramolecular hydrogen bonds, but subject to some interaction with CCl_4 molecules) and the low frequency component at $3605._9$ cm^{-1} is due to intramolecular OH...π interaction. Since molecular models and the relative peak heights in the absorption spectrum show that OH...π bonding is favoured in this system because of the easy access of the OH groups to the aromatic π-electrons, knowledge of ΔH for the trans-gauche equilibrium is important for the interpretation of the spectra of more complicated hydroxy compounds.

The enthalpy difference between trans and gauche forms of 2-phenylethanol is -1.04 ± 0.02 kcal/mole, based on the temperature dependence of the

* From the Ph.D. Thesis of H.D. Mettee, University of Alberta, Calgary, (1964). Part VIII in the series "Spectroscopic Studies of Alcohols".

absorbance ratio for the two OH bands (Fig. 1(b)). The corresponding rotational entropy difference is 3.6 e.u., estimated from the intercept of the above plot, assuming that the extinction coefficient ratio for the two OH bands remains constant and equal to unity over the temperature range involved. However, the second assumption is questionable.

The enthalpy difference reported here differs considerably from two estimates previously made in the literature. Goldman and Crisler (4) estimated the interaction in 2-phenylethanol to be -0.88 kcal/mole from the OH frequency shift. This value is low because Badger's rule does not necessarily apply to intramolecular hydrogen bonds. On the other hand, Schleyer et al (1) placed ΔH at -1.4 kcal/mole, which appears to be too large.

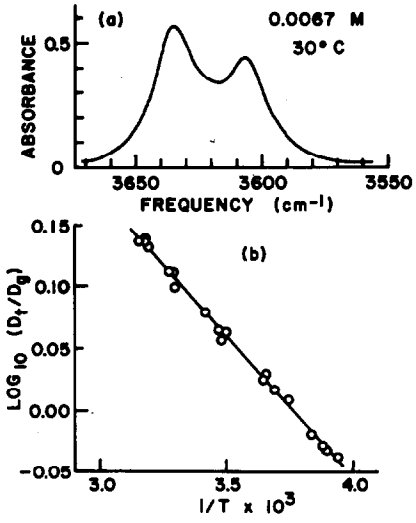

Fig. 1 (a) Fundamental OH stretching bands of 2-phenylethanol in dilute CCl_4 solution. Path length 2.00 cm. (b) Temperature dependence of the OH peak absorbance ratio in 2-phenylethanol.

Oki and Iwamura (6) have attempted to make very specific conformational assignments for 2-phenylethanol on the basis of substituent effects in the aromatic ring. For the intramolecularly hydrogen bonded form they favour a gauche conformation with the OH directed toward the C_1-C_2 bond of the aromatic ring, with some contribution from a conformation with the OH directed toward the π-electrons at C_2 in the aromatic ring. By assuming Lorentzian band contours, the same authors also resolved the 2-phenylethanol spectrum mathematically in the fundamental OH stretching region into three overlapping components (3), of which they assigned the two of highest frequency to rotational isomerism about the C-O bond (with the C-O bond trans to the phenyl ring on the ethanol skeleton). This mathematical resolution could only be done with considerable uncertainty, particularly for the central band of lowest intensity. Since current evidence indicates that infrared absorption bands in condensed media are in general more closely described as hybrids of Lorentzian and Gaussian envelopes (7), it is doubtful whether the forced resolution into three components by Oki and Iwamura is justified. On the basis of the ring substituent effect on frequency shifts in the 2 ν_{OH} region Goldman and Crisler (4) favoured intramolecular hydrogen bonding to C_1 of the ring.

The enthalpy difference reported in this note is considered to be that between "free" OH groups (perhaps in several spectroscopically indistinguishable conformations) and intramolecularly OH..π bonded groups, without reference to the orientation of the OH group with respect to the π-electron distribution. Although this value does not measure the OH...π hydrogen bond energy directly because of differences in other non-bonded interactions between the trans and gauche forms, it does show that this type of intramolecular hydrogen bond is a major factor stabilizing the gauche conformation.

The details of the experimental procedure employed have been described (8).

ACKNOWLEDGEMENT: This investigation was supported financially by the National Research Council of Canada.

REFERENCES

1. P. von R. Schleyer, C. Wintner, D.S. Trifan, and R. Bacskai, Tetrahedron Letters No. 14, 1 (1959).
2. A.W. Baker and A.T. Shulgin, J. Am. Chem. Soc. 80, 5358 (1958).
3. M. Oki and H. Iwamura, Bull. Chem. Soc. Japan 33, 1600 (1960, and other papers in this series.
4. I.M. Goldman and R.O. Crisler, J. Org. Chem. 23, 751 (1958).
5. J. Pitha and M. Horak, Coll. Czech. Chem. Comm. 25, 1586 (1960).
6. M. Oki and H. Iwamura, Bull. Chem. Soc. Japan 32, 1135 (1959).
7. K.S. Seshadri and R.N. Jones, Spectrochim. Acta. 19, 1013 (1963).
8. P.J. Krueger and H.D. Mettee, Can. J. Chem. 42, 326, 340 (1964).