A STUDY OF *cis - trans* ISOMERISM OF BENZALIDE AND THIOBENZANILIDE

B. BOGDANOV and I.PETROV
Institute of Chemistry, Faculty of Science-Skopje,
91000 Skopje, Macedonia, Yugoslavia

ABSTRACT

The conformations of the benzanlide and thiobenzanilide are studied using IR spectral data and Extended Huckel MO calculations. The results indicate that the benzanilide in CCl₄ dilute solution exist only in a *trans*-conformation , while the thiobenzanilide exist in a *cis-trans* equilibrium . The observed relative stabilities of the *cis*-thiobenzanilide can be explained on the basis of the calculated torsional barriers around the thiocarbonyl-nitrogen bond .

INTRODUCTION

The structure behavior of the amides and thioamides have been the subject of much investigation using the spectroscopic and theoretical studies [1-6] . A more detailed study of their configurations is of importance in any attempt of structure - activity correlation .

The benzanilide (I) and thiobenzanilide (II) could possibly take the *trans* - and *cis* - isomeric forms (Fig. 1) . Φ_1 and Φ_2 are torsional angles between the plane of the functional group and plane of the phenyl rings bound to N and C atoms.The partially double bond character of the C-N bond from the Ph-C(X)-NH-Ph (X=O or S) which is due to the delocalization of the electronic pair at the nitrogen atom determines the hindered rotation around this
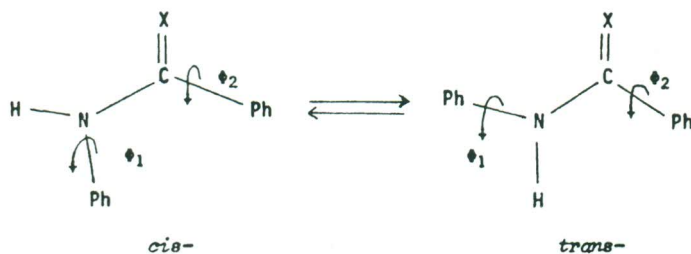
Fig. 1. Molecular conformations of benzanilide (I, X=O) and thiobenzalide (II, X=S) . The *cis*- and *trans*-planar conformations ($\Phi_1 = \Phi_2 = 0°$) are shown.

bond and the possibilities for a relative stabilization of different conformational isomers . Suzuki et al. [1] examined a series of thioformanilides and thioacetanilides and showed that the thioformanilides have predominantly a *cis*-conformation while the thioacetanilides exist in both *cis* and *trans* forms. In this respect the thioanilides evidently differ from anilides which normally have a *trans*-conformation . This difference is attributed on increased steric repulsion between the phenyl ring and the sulfur atom in the thioamides . The torsional barriers in thioamides are in general 0.04-0.13 eV/mol higher than in corresponding amides [4] .

In the present work IR spectral data and Extended Huckle MO (EHMO) calculations for the existence of conformational isomerism in benzanilide and thio benzanilide are analysed .

EXPERIMENTAL

Infrared spectra

The benzanilide and the thiobenzalide were synthesized using known method [7] .The infrared spectra were recorded on a Perkin-Elmer 580 IR Spectrophotometer . The benzanilide and the thiobenzanilide as dilute solution in CCl_4 (at concentrations $1.2 \cdot 10^{-3}$M and $1.3 \cdot 10^{-3}$M , respectively) were recorded . The IR spectra in the N-H stretching frequencies range are shown in Fig. 2 .
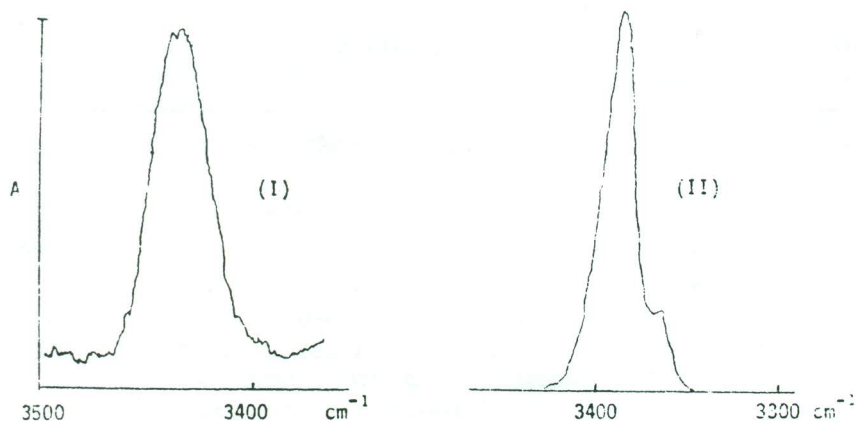
Fig. 2. IR spectrum of benzanilide (I) and thiobenzanilide (II) in CCl₄.

Method of calculations

The total energies were calculated by means of EHMO method using QCPE No 358 . Adopted values of integrals an parametrization are the same as in ref. [8] . The sulfur $3d$ orbitals were included in the basis set . The bond lengths and angles were set a values given by X-ray analysis [9] ; regular benzene rings are assumed .

RESULTS AND DISCUSSION

In the infrared spectrum of benzanilide in carbon tetra chloride dilute solution , the N-H stretching vibration appears as a single monomeric band at 3440 cm^{-1} , while the spectrum of thiobenzalide gives rise to two monomeric bands , a strong one at 3390 cm^{-1} and a weak one at 3365 cm^{-1} (Fig. 2) . The appearance of two bands in thiobenzalide indicates that it exist in a *cis-trans* equilibrium . The strong band belongs to *trans-* and the weak to *cis-* configuration .

The conformational preference exhibited by these molecules is clearly governed by the relative importance of two factors , the π-interactions which tend to keep the molecules planar (the conjugative factor), and the non-bonding interactions which may be alleviated by deviation from planarity (the steric factor) . We

Table 1

Torsional barriers and potential constants (in eV) of benzanilide
(I) and thiobenzanilide (II)

Molecule	conformation Φ_1, Φ_2 (deg.)	cis-trans barrier	V_1	V_2	V_3
I	90, 90[a]	0.999	-0.105	1.094	-0.085
II	90, 90[a]	1.130	-0.013	1.176	-0.079
I	90, 90[b]	1.835	1.568	0.879	0.342
II	90, 90[b]	2.085	1.857	0.923	-0.396

[a]Most stable cis-conformation (see Fig. 1).
[b]Most stable trans-conformation (see Fig. 1).

have carried out MO calculations employing EHMO method to estimate
the relative stabilities and the barrier highs to rotation . The
torsional barriers around C-N bond for benzanilide and
thiobenzanilide are presented in Table 1.

The expansion to a Fourier series of the potential function

$$V(\Phi) = \sum \frac{1}{2} V_{Ni} (1 - \cos N_i \Phi)$$

deserves some interest since it allows various physical effects on
the mechanism of rotational barriers to be separated   [10] . In
particular , the physical effects reflected by the potential
constants V_i for the present compounds are the interaction of
local dipole and steric hindrance (V_i), the tendency to adopt an
uniplanar conformation in order to maximize conjugative stability
(V_2), and the bond-bond repulsion (V_3) . For most stable cis-
conformation, the results prove that the two-fold component (Table
1) for benzanilide and thiobenzanilide is most important and
largely responsible for the rotational barrier. Furthermore, the V_1
is more important than V_3, and although smaller than V_2, plays a
decisive role in assessing the relative stabilities of the cis-and

trans-conformations. The energy barrier and potential constant V_2 of benzanilide are smaller than those of thiobenzanilide, indicating less mesomeric inter action between oxygen and C-N bond, than those between sulfur and C-N bond. However, as can be seen from Table 1,the most stable *trans*-conformation of benzanilide and thiobenzanilide have V_1 values greater than V_2 indicating that the steric factor play dominant role in the total torsional barrier of those molecules.

ACKNOWLEDGEMENT

REFERENCES

1   I. Suzuki, M. Tsuboi, T. Shimanouchi, S. Muzishima, Spectrochim. Acta, 16 (1960) 471.

2   G. Isaksson and J. Sandstrom, Acta Chem. Scand., 21 (1967) 1605.

3   C. N. Rao, K. G. Rao, A. Goel and D. Balasubramanian, J. Chem. Soc. (A), (1971) 3077.

4   C. Piccinni-Leopardi, O. Fabre, D. Zimmermann and J. Reissue, Can. J. Chem. 55 (1977) 2649.

5   J. Sandstrom, Tetrahedron Lett., 7 (1979) 639.

6   I. Petrov and O. Grupce, J. Mol. Struct., 115 (1984) 481.

7   O. Grupce and I. Petrov, J. Mol. Struct., 115 (1984) 119.

8   V. Galasso, G. De Alti and A. Bigotto, Tetrahedron, 27 (1970) 6151.

9   J. Zabicky, The Chemistry of Amides, Internecine Publishes, London 1970,p.4 and 387.

10   L. Radom, W. J. Hehre and J. A. People, J. Am. Chem. Soc., 94 (1972) 2371.