Russian Journal of General Chemistry, Vol. 73, No. 6, 2003, pp. 996–997. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 6, 2003, pp. 1053–1054.
Original Russian Text Copyright © 2003 by Sarapulova, Rozentsveig, Rozentsveig, Levkovskaya .

LETTERS TO THE EDITOR

Unusual Molecular Structure of *N*-(2,2-Dichloro-1-hydroxy-2-phenylethyl)-4-chlorobenzenesulfonamide

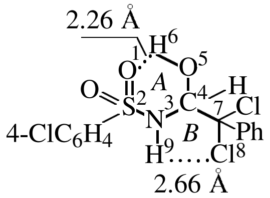
G. I. Sarapulova, G. N. Rozentsveig, I. B. Rozentsveig, and G. G. Levkovskaya

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, Russia

Received February 27, 2002

Earlier we synthesized a series of derivatives of highly electrophilic *N*-(2,2-dichloro-2-phenylethylidene)arenesulfonamides [1]. The available and important synthon of this series, *N*-(2,2-dichloro-1-hydroxy-2-phenylethyl)-4-chlorobenzenesulfonamide (**I**), exhibits IR characteristics different from those of isostructural analogs and model *N*-methylmethanesulfonamide (**II**) [ν(NH) 3409, $\nu_{as}(SO_2)$ 1340 cm^{-1}] [2]: very low values of ν(NH) (3350 cm^{-1}), $\nu_{as}(SO_2)$ (1315 cm^{-1}) and ν(OH) (3570 cm^{-1}) in $CHCl_3$.

The characteristic reorganization of the $\nu(SO_2)$, ν(NH), ν(OH), and δ(C–Cl) bands in the IR spectra of compound **I** in 1,1,2,2-tetrachloroethane over a wide temperature range (20–120°C) suggests formation and subsequent cleavage of intramolecular hydrogen bonds involving the corresponding fragments. Therewith, the ν(OH) and ν(NH) bands are observed at 3610 and 3420 cm^{-1}, respectively, and the $\nu_{as}(SO_2)$ band, at 1358 cm^{-1}.



I

Interactions of amide **I** with pyridine, DMSO, and THF, too, involve cleavage of intramolecular hydrogen bonds, but simultaneously new intermolecular hydrogen-bonded complexes involving OH (3200 cm^{-1}) and NH (3150 cm^{-1}) groups are formed. The AM1 calculations [3] of compounds **I** and **II** revealed two shortened intramolecular contacts in the former: between sulfone O^1 and H^6, as well as between H^9 and Cl^8, much shorter than the sums of van der Waals radii. The $O^1 \cdots O^5$ distance is 2.7 Å. The $S^2N^3C^4O^5$ and $O^1S^2N^3C^4$ torsion angles are –58.5 and 1.03°, respectively. The $H^9N^3C^4C^7$ and $N^3C^4C^7Cl^8$ torsion angles are –5.63 and –64.4°, respectively. The endocyclic bond angles in pseudocycles *A* and *B* in amide **I** are much decreased compared with «ideal» [4] and those in model compound **II**: $S^2N^3C^4$ 122°, $C^4O^5H^6$ 107.3°, and $C^4C^7Cl^8$ 112.2°, which favors mutual stabilization of intramolecular hydrogen bonds. The intramolecular hydrogen-bonded preudocycles have a common central bond C–N incorporated in an almost planar $O^1S^2N^3C^4C^7$ pentad, and also stabilize each other.

Comparative analysis of the orders, and especially π-orders (P_π) of bonds in model compound **II** and two structures of compound **I**, with two intramolecular hydrogen bonds and without them, points to a considerable electron delocalization in the hydrogen-bonded form of compound **I**. Thus, the P_π values for the hydrogen-bonded form in the bond series S^2–N^3, N^3–S^4, S^4–O^5, S^2=O^1 form the series 0.083, 0.047, 0.066, 0.346, and the respective values for the hydrogen-nonbonded form are 0.077, 0.059, 0.084, 0.336. Moreover, lengthening of the S=O bond from 1.407 to 1.416 Å is observed and alternation of other bond lengths, specifically, C–H from 1.438 to 1.446 Å and O–H from 0.967 to 0.972 Å.

According to calculations, the hydrogen-bonded structure of compound **I** is preferred over hydrogen-nonbonded by 33.06 kJ/mol. The energies of noncomplementary hydrogen bonds ΔH (kJ/mol), experimentally estimated by us from the temperature dependences of the optical densities of the ν(NH) and ν(OH) bands for free and bonded groups in $C_2H_2Cl_4$, are 17.55 for pseudocycle *A* and 9.19 for pseudocycle *B*.

The spectral data and calculations are consistent with the stereochemical features of compound **I**, which show up in the slightly increased π-order of the N–S bond compared with those in usual sulfonamides,

1070-3632/03/7306-0996$25.00©2003 MAIK "Nauka/Interperiodica"

where conjugation in the SO_2N group is weak. The resulting data provide convincing evidence for the concept of synergism of hydrogen bonding and delocalization of electron density [5, 6].

REFERENCES

1. Levkovskaya, G.G., Drozdova, T.I., Rozentsveig, I.B., and Mirskova, A.N., *Usp. Khim.,* 1999, vol. 68, no. 7, p. 638.
2. Pikkarainen, L., *Finn. Chem. Lett.,* 1980, no. 4, p. 109.
3. Dewar, M.J.S., Zoebisch, E.G., Healy, E.F., and Stewart, J.J.P., *J. Am. Chem. Soc.,* 1985, vol. 107, no. 13, p. 3902.
4. Gordon, A.J. and Ford, R.A., *The Chemist's Companion,* New York: Wiley, 1972, p. 540.
5. Gilli, G., Bellucci, F., Ferretti, V., and Bertolasi, V., *J. Am. Chem. Soc.,* 1989, vol. 111, no. 3, p. 1023.
6. Gilli, P., Bertolasi, V., and Ferretti, V., *J. Am. Chem. Soc.,* 1994, vol. 116, no. 3, p. 909.