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B.A. Trofimov on the 65th Anniversary of His Birth

Quantum-Chemical Study of Methyl Phenyl Sulfide

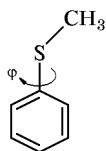
Yu. L. Frolov and A. V. Vashchenko

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: yulf@irioch.irk.ru

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Abstract—Steric and electronic structure of the methyl phenyl sulfide molecule was studied by nonempirical quantum-chemical methods. The calculations were performed by the B3LYP and MP2 procedures with account taken of electronic correlation using extended 6-311++G(3d,p) basis sets. The use of a balanced method and basis set allowed us to avoid discrepancy between the experimental and calculated data reported by other authors. The results confirmed coplanar orientation of the C–S–C fragment and the benzene ring, which follows from most experimental studies.

Despite numerous studies of methyl phenyl sulfide by various physicochemical methods and theoretical methods based on both semiempirical and nonempirical calculations, some problems concerning steric and electronic structure of its molecule still remain unsolved.



Most experimental studies revealed the presence of two conformers, planar and orthogonal. The planar conformer is likely to be the most stable. Various experimental procedures give different populations of one or another conformer. According to the estimates on the basis of photoelectron spectra [1], the fraction of a planar conformer is about 90%. An analogous conclusion was drawn by Schweig and Thon [2] who studied temperature dependence of the photoelectron spectrum of methyl phenyl sulfide in the range from 20 to 500°C. The authors estimated the fraction of the planar conformer at ~79% (20°C). Analysis of the ¹H and ¹³C NMR spectra of PhSMe in the nematic phase and of the data of UV and microwave spectroscopy [3] gives a 50–85% fraction of the planar form. A similar value (86%) was obtained by Ratovskii and co-workers [4–6] by analysis of the IR and UV

spectra. Velino *et al.* [7] examined the microwave spectra of methyl phenyl sulfide and revealed the presence of the planar conformer as the only one. The results of ¹³C NMR study of the effect of substituents in the *para* position on the conformation of the methylsulfanyl group [8, 9] revealed a dependence of the predominant conformer on electronic properties of the substituent: donor substituents increase the fraction of the orthogonal isomer, while acceptor groups favor the planar structure. Despite different estimates of the population of the orthogonal conformer, obtained by different methods, all these prefer the planar conformer as the most energetically favorable. The data of gas electronography obtained by Zaripov [10] are an exception. The author concluded that the methyl phenyl sulfide molecule is essentially nonplanar: the C_{sp²}SC_{sp³} angle is 45 ± 10°.

The results of quantum-chemical calculations are characterized by greater discrepancies concerning the most favorable conformer of methyl phenyl sulfide. Semiempirical calculations (AM, PM3) and nonempirical methods with the use of STO-3G and STO-3G* basis sets [11], as well as BLYP, B3LYP, and B3P86 calculations, predict greater stability of the planar conformer [12, 13]. MNDO and nonempirical Hartree–Fock approximations with D95*, 6-31G*, 6-31G**, 6-31++G**, and 6-311G** basis sets together with Moeller–Plesset calculations (MP2, MP3, MP4) with account taken of electronic correlation give preference

to the orthogonal conformer [12, 13]. Bzhezovskii *et al.* [13] believe that the different results obtained in the Hartree–Fock and Moeller–Plesset approximations, on the one hand, and by the DFT methods, on the other, could not be explained in terms of the geometric parameters but originate from different ways of consideration of electronic correlation, which should affect determination of stationary points on the potential function for internal rotation in molecules characterized by a low rotation barrier. We believe that the main factor responsible for the observed difference in the theoretical results is insufficient size of the basis set and disagreement between the calculation procedure and the basis set used. For example, most calculations by Bzhezovskii *et al.* [12, 13] were performed with the 6-31G* or 6-31G** basis set. No calculations in a more extended than 6-311G** basis set have been reported, though this basis set is insufficient for molecules containing 3rd Period elements.

Attempts [12, 13] to meet a compromise between the method and the basis set frequently rested on computation time, so that no optimal relation between the calculation procedure and the basis set was found. While analyzing molecules with a low rotation barrier, such an imbalance could lead to improper results. In order to elucidate the effect of the method and basis set on the position of stationary points for methyl phenyl sulfide and estimate how the results obtained with an extended basis set correlate with the experimental data, we performed calculations using the 6-311++G(3*d,p*) basis set with and without account taken of electronic correlation. For comparison, we also used the 6-311G(2*d,p*) basis set including 2*d* functions. The potentials of internal rotation about the C_{sp²}–S bond were determined through a step of 10 deg with full optimization of the other parameters. The results are given in table.

Apart from the effect of the basis set on the shape of the potential curve, we examined the effect of the solvent by the Onsager method [14]. The results are shown in figure. All methods considering electronic correlation showed a surprising consistency. Our estimates indicated that the planar structure of methyl phenyl sulfide is preferred. The opposite results were obtained in the Hartree–Fock approximation, according to which the orthogonal conformer is more favorable. This contradicts both theoretical (B3LYP and MP2) and experimental data. It should be noted that inclusion of *d*, 2*d*, or 3*d* orbitals exerts no appreciable effect on the shape of the potential curve; nevertheless, *d* functions should necessarily be taken into account while studying molecules containing 3rd Period elements. One more important thing is

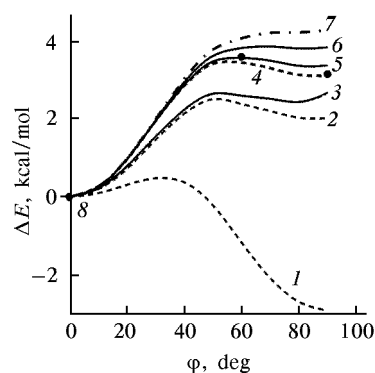
Methods and basis sets used in the calculation of dipole moments for media with different dielectric constants

No.	Method/basis set	μ_{calc} , ^a D	Dielectric constant ϵ
1	HF/6-311++G(3 <i>d,p</i>)	1.48	1
2	B3LYP/6-311G(2 <i>d,p</i>)	1.34	1
3	B3LYP/6-311++G(<i>d,p</i>)	1.39	1
4	B3LYP/6-311++G(3 <i>d,p</i>)	2.08	35.9
5	B3LYP/6-311++G(3 <i>d,p</i>)	1.91	7.32
6	B3LYP/6-311++G(3 <i>d,p</i>)	1.59	2.23
7	B3LYP/6-311++G(3 <i>df,p</i>)	1.31	1
8	MP2/6-311++G(3 <i>d,p</i>)	1.46	1

^a $\mu_{\text{exp}} = 1.31$ D [15].

consideration of diffuse functions, which was clearly neglected by Bzhezovskii *et al.* [12, 13]. Imbalance between the calculation procedure and the basis set and neglect of diffuse functions could lead to a considerable disagreement between the theoretical and experimental data.

Calculations by the DFT and MP2 methods revealed a second minimum on the potential curve for internal rotation about the C_{sp²}–S bond, which is located in the range from 80 to 100°. In keeping with the generally accepted views, conformation of methyl phenyl sulfide is determined by two main factors: *p*, π conjugation between the sulfur atom and the aromatic fragment and steric interaction between the methyl protons and *ortho*-protons of the benzene ring. Presumably, the latter factor should not be significant, for the barrier to rotation of the methyl group is much



Potential curves for internal rotation about the C_{sp²}–S bond in methyl phenyl sulfide, calculated by different methods using different basis sets for media with different dielectric constants. The numbers of the curves correspond to the method/basis set numbers in table; black circles refer to the results of MP2/6-311++G(3*df,p*) calculations.

lower than the barrier to rotation about the C_{sp^2} -S bond. Steric strains caused by rotation about the C_{sp^2} -S bond should readily be compensated by rotation of the CH_3 group. Therefore, the main factor responsible for mutual arrangement of the aromatic ring and methylsulfanyl group is p,π conjugation between the sulfur atom and the aromatic fragment. However, it is difficult to explain the appearance of the second energy minimum on the basis of classical views on the structure of lone electron pair on the sulfur atom and mechanism of p,π conjugation between the sulfur atom and the aromatic ring. Expansion of the potential function for internal rotation about the C_{sp^2} -S bond into a Fourier series shows that the first three terms of the series give the main contribution. The fact that conformations of the methyl phenyl sulfide molecule with the methyl group turned through angles of 0 and 180° with respect to the aromatic ring are indistinguishable leads to domination of the first, second, and sixth terms of the Fourier series. The latter term is responsible for appearance of energy minima at 30 and 90° and an energy maximum at about 60° . Comparison of the experimental dipole moment of methyl phenyl sulfide with those calculated with the use of various basis sets shows a good reproducibility with most of the latter (see table). The best agreement was achieved with the B3LYP/6-311++G(3df,p) basis set.

REFERENCES

- Dewar, P.S., Ernstbrunner, E., Gilmore, J.R., Godfrey, M., and Mellor, J.M., *Tetrahedron*, 1974, vol. 30, no. 15, p. 2455.
- Schweig, A. and Thon, N., *Chem. Phys. Lett.*, 1981, vol. 81, no. 3, p. 615.
- Emsley, J.M., Longeri, M., Veracini, C.A., Catalano, D., and Pedulli, G.F., *J. Chem. Soc., Perkin Trans 2*, 1982, no. 10, p. 1289.
- Panov, A.M., Ratovskii, G.V., Chuvashov, D.D., and Shivernovskaya, O.L., *Zh. Obshch. Khim.*, 1983, vol. 53, no. 3, p. 517.
- Ratovskii, G.V., Shivernovskaya, O.L., Panov, A.M., and Aliev, I.A., *Zh. Obshch. Khim.*, 1989, vol. 59, no. 10, p. 2273.
- Shivernovskaya, O.L., Ratovskii, G.V., Kondratenko, N.V., and Boiko, V.N., *Ukr. Khim. Zh.*, 1992, vol. 58, no. 7, p. 687.
- Velino, B., Melandri, S., Caminati, W., and Favero, P.G., *Gazz. Chim. Ital.*, 1995, vol. 125, no. 8, p. 373.
- Kalabin, G.A., Bzhezovskii, V.M., Kushnarev, D.F., Trofimov, B.A., and Chmutova, G.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, no. 5, p. 1002.
- Bzhezovskii, V.M., Kalabin, G.A., Aliev, I.A., Donskikh, V.I., and Trofimov, B.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, no. 7, p. 1525.
- Zaripov, N.M., *Zh. Strukt. Khim.*, 1976, vol. 17, no. 4, p. 741.
- Bzhezovskii, V.M., Il'chenko, N.N., Kulik, N.I., and Yagupol'skii, L.M., *Russ. J. Gen. Chem.*, 1997, vol. 67, no. 10, p. 1592.
- Bzhezovskii, V.M., Kapustin, E.G., and Il'chenko, N.N., *Russ. J. Gen. Chem.*, 2000, vol. 70, no. 5, p. 745.
- Bzhezovskii, V.M., Kapustin, E.G., Il'chenko, N.N., Kulik, N.I., and Gorb, L.G., *Russ. J. Gen. Chem.*, 2000, vol. 70, no. 11, p. 1766.
- Onsager, L., *Electric Moments of Molecules in Liquids*, New York: 1936, vol. 58, p. 1486.
- Baliah, V. and Uma, M., *Tetrahedron*, 1962, vol. 19, p. 455.