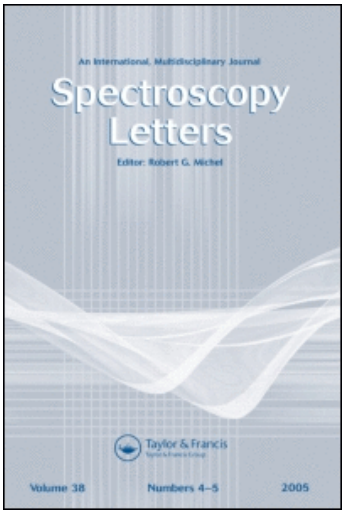

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INFRARED SPECTRA SIMULATION FOR SOME SULFONAMIDES BY USING SEMI-EMPIRICAL METHODS

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ABSTRACT

Infrared (IR) spectra of sulfadimethoxine (SDMX), sulfamethoxazole (SMX) and sulfanilamide (SD) have been simulated by a set of the semi-empirical methods supplied by the HyperChemTM package. Before the IR simulations, the initial geometries of the molecules were built by means of X-ray diffraction data and standard parameters and full geometry optimizations were performed with the unrestricted Hartree-Fock basis, Polak–Ribiere conjugate gradient algorithm. It was found that IR spectra simulated by the semi-empirical method MINDO3 gives the best match to the observed spectra and also this method provides the best linearity between calculated and experimental wave numbers (with a correlation coefficient of 0.99780). The certain assignment of the most useful vibrational modes of sulfonamides were determined by using semi-empirical methods. At the

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same time, none of the methods is able to predict infrared intensities and a spectral intensity pattern.

Key Words: Sulfonamides; IR spectra; X-ray diffraction; Semi-empirical methods

INTRODUCTION

Sulfonamides have been extensively used in medicine for their antibacterial properties and their metal complexes have gained popularity for the control of infections in extensive burns. Recently, we studied the vibrational spectra of sulfadimethoxine (SDMX), sulfamethoxazole (SMX), sulfanilamide (SD) and their some metal complexes[1–3]. Our interest in metal chelates of sulfa drugs was inspired by the fact that they were more bacteriostatic than the drugs themselves. For the characterization of the metal complexes, the certain assignment of the most important vibrational modes of sulfonamides should be determined. Ab initio and semi-empirical quantum mechanical methods are quite common in normal coordinate analysis and band assignment. They are at present widely used for simulating infrared spectra. So far, only the molecular mechanics conformational analysis of N-3-pyridinylmethanesulfonamide and the assignment of its IR spectrum supported by Hartree-Fock ab initio calculations of the fundamental vibrations had been reported by Dodoff[4]. As is known, powerful computers are necessary for running ab initio calculations and IR spectra simulations take much longer as compared to the semi-empirical ones.

In this study, we have used semi-empirical methods instead of ab initio ones. The main aim of this paper is to estimate the quality of IR spectra calculations for SDMX, SMX and SD and to confirm the assignments of the most important vibrational modes by four semi-empirical methods (PM3, AM1, MNDO and MINDO3).

EXPERIMENTAL

Infrared spectra of the samples were recorded on a Perkin-Elmer 621 spectrometer using the KBr technique, in the region 4000–500 cm^{-1}, which were calibrated by polystyrene.

The proposed structures of the samples were optimised and their infrared spectra generated based on molecular mechanics and semi-empirical calculations using Hyperchem 5 Molecular Visulation Simulation

program[5]. The initial geometries of the molecules were built by means of X-ray diffraction data and standard parameters, then optimised by Polak-Ribiere geometrical optimization, RMS gradient $0.008\,\text{kcal}\,\text{Å}^{-1}\,\text{mol}^{-1}$. Geometry optimizations based on molecular mechanics (using MM+ force field) and semi-empirical quantum mechanical calculations (using PM3, AM1, MNDO and MINDO3) were used to find the molecular structures that represent a potential energy minimum. All the calculations refer to isolated molecules in vacuo. For the optimised structures, the infrared spectra were generated using PM3, AM1, MNDO and MINDO3 methods.

RESULTS AND DISCUSSION

Firstly, the initial geometries of the molecules were built by means of X-ray diffraction data[6] and standard parameters then optimised by using the MM+ program. Then, the last molecular conformations of the molecules were obtained by the global energy minimum. The molecular geometries of the samples obtained from this study were illustrated in Figs. 1a, b and c.

The simulated versus experimental IR spectra for SDMX, SMX and SD are presented in Figs. 2–4, respectively; and the selected fundamental wave numbers are listed in Table 1. As seen from Table 1, $\nu_{sym.}(SO_2)$ vibration observed in the experimental IR spectrum of SMX could not be identified in the simulated counterpart by using MNDO method, and therefore was omitted.

The assignment of the calculated wave numbers was aided by animation option of the HYPERCHEM programme which gives a visual presentation of the shape of the vibrational modes. In our previous studies, the assignments of the vibrational modes had been taken from literature data for molecules containing related structural fragments[7–11]. In the present study, the assignments of the individual vibrations were confirmed by simulating IR spectra and no coupled modes were selected for the comparison. Comparison with the experimental data shows that the spectra simulated by MINDO3 gives evidently the best match to their experimental counterparts. As seen from Table 1, the best agreement between the experimental and calculated frequencies for ν_{NH} and δ_{NH} can be obtained by AM1 method. However, if to omit these vibrations in the case of MINDO3, for the remaining values, this method gives relatively good results.

A linearity between the experimental and calculated wavenumbers can be derived from the same plots in Fig. 5 as correlation coefficients. According to the values presented in this figure, the best is MINDO3 ($cc = 0.99780$), although even ($cc = 0.98465$) (the lowest, for PM3) can be

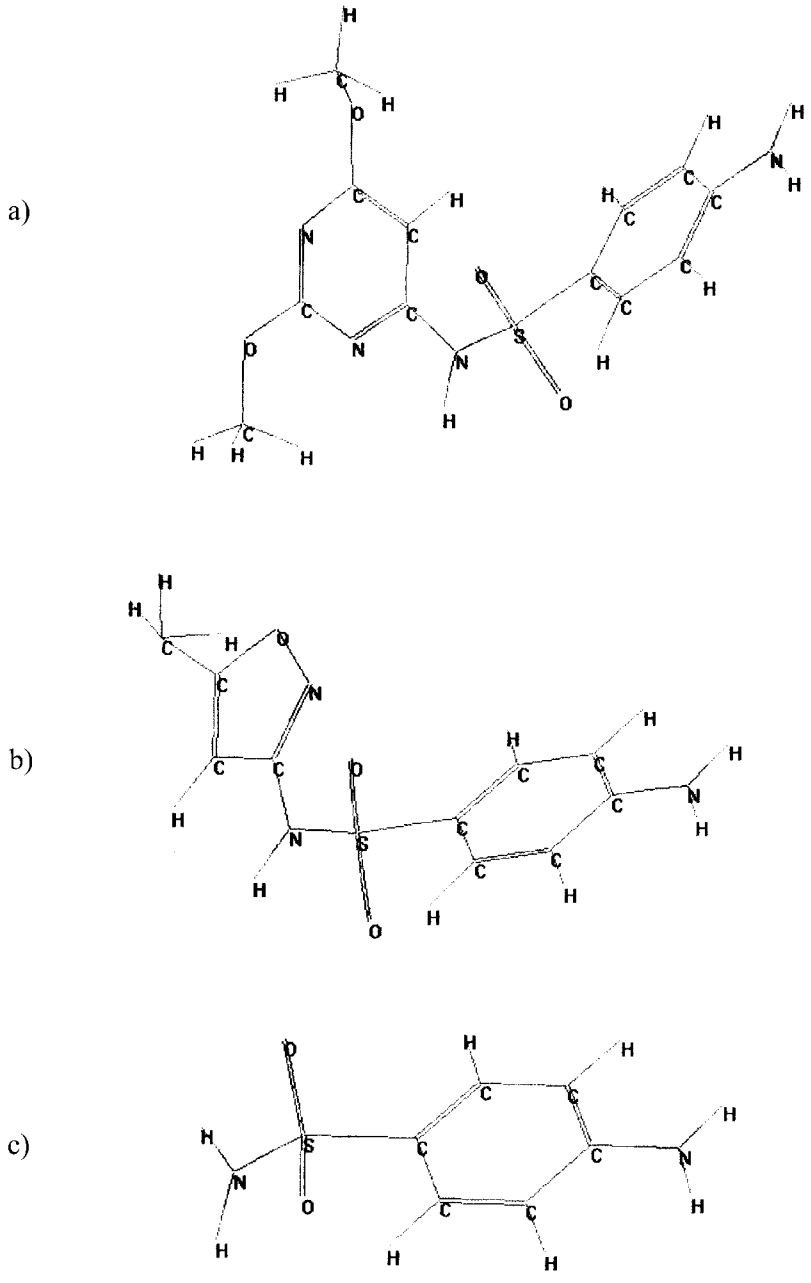

Figure 1. The molecular geometries of a) SDMX, b) SMX, c) SD.

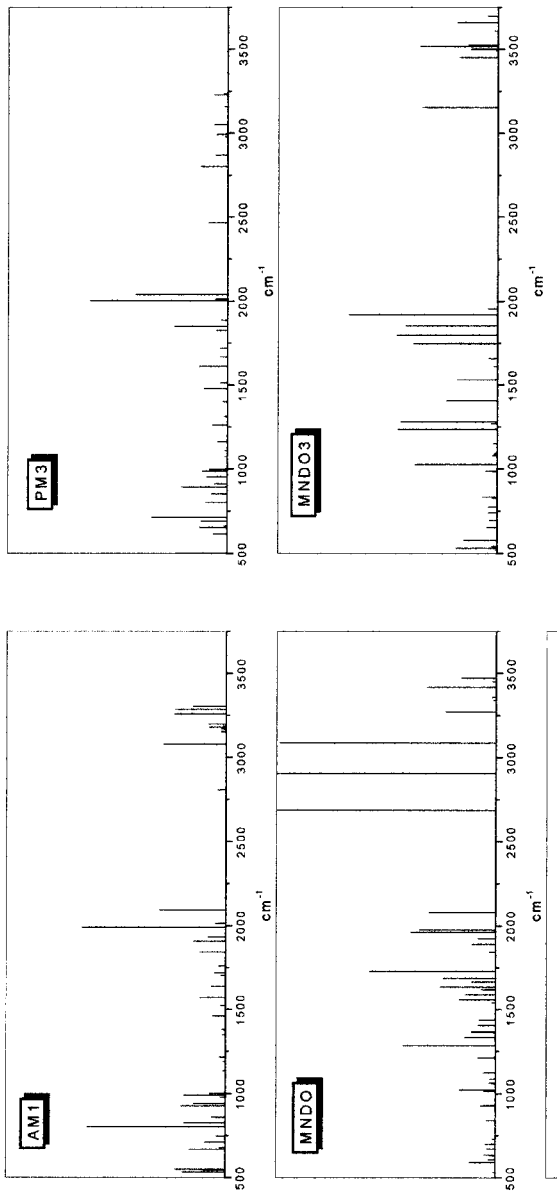

Figure 2. Simulated and experimental IR spectra for SDMX.

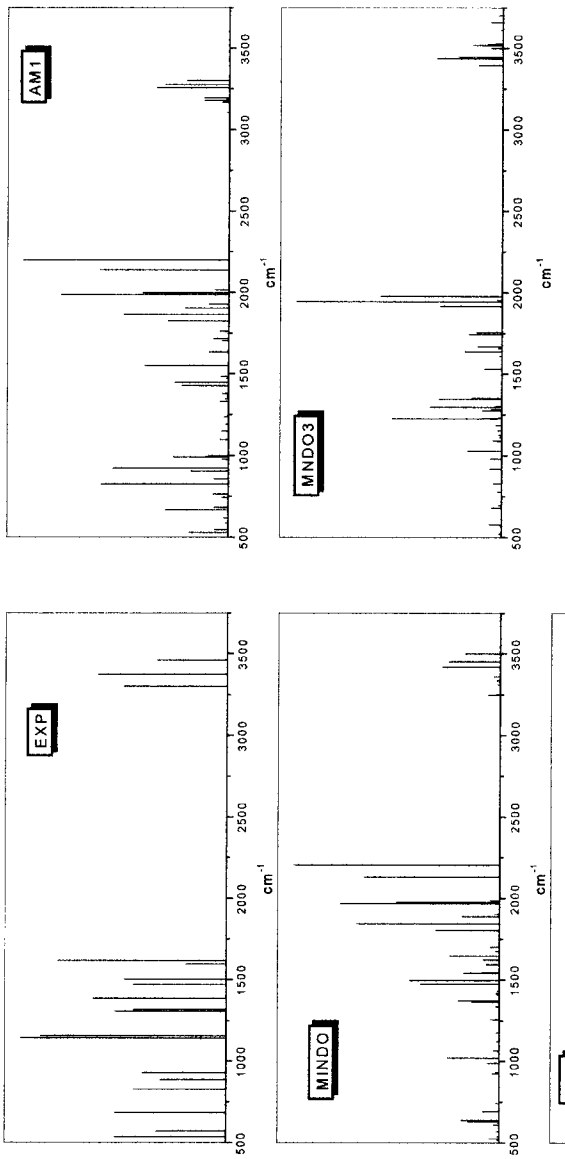

Figure 3. Simulated and experimental IR spectra for SMX.

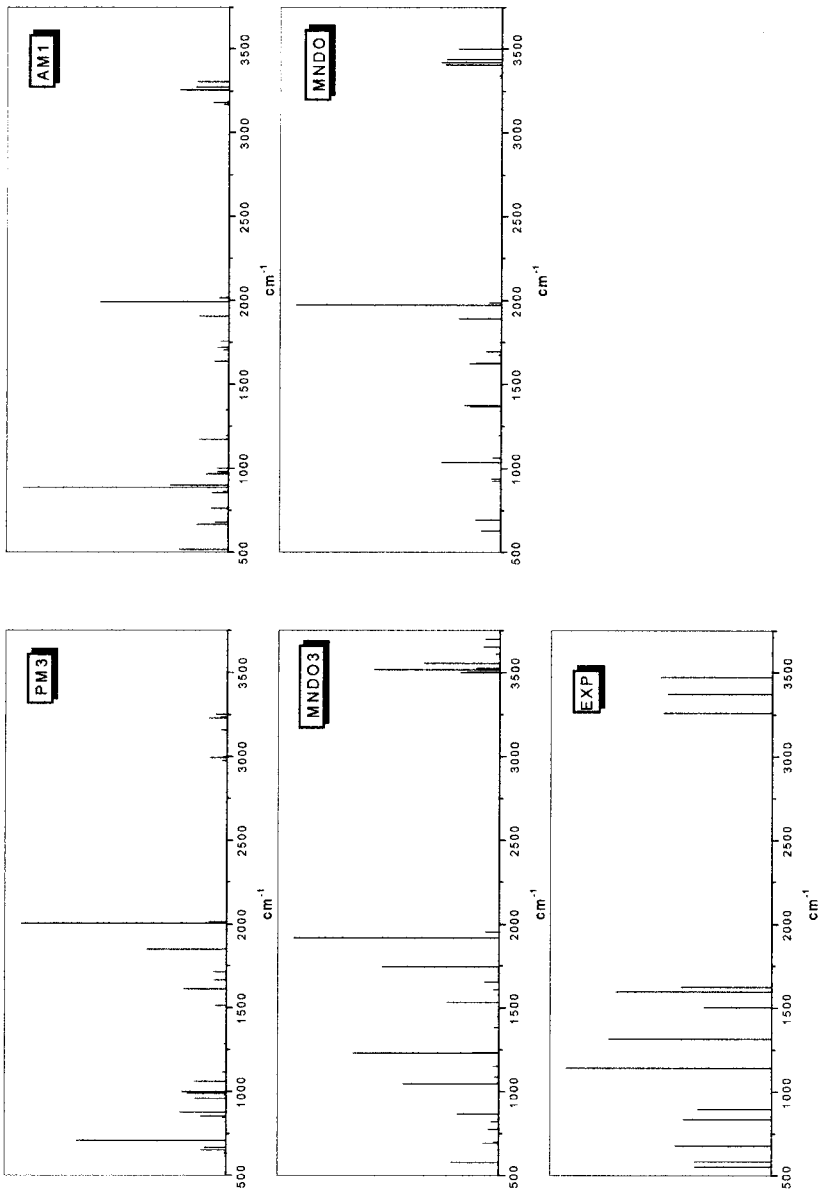

Figure 4. Simulated and experimental IR spectra for SD.

Table 1. Selected Experimental (from [1–3]) and Calculated Wave Numbers (cm^{-1}) and Their Assignments for Some Sulfonamides Obtained by AM1, PM3, MINDO3, and MNDO Semi-empirical Methods

Assignments	Experimental	AM1	PM3	MINDO3	MNDO
Sulfanilamide					
$\nu_{asym.}(NH_2)$aniline	3474	3304	3237	3699	3500
$\nu_{sym.}(NH_2)$aniline	3372	3260	3157	3611	3419
$\nu_{sym.}(NH_2)$sulfonamide	3260	3274	3252	3559	3405
$\delta(NH_2)$aniline	1627	1719	1514	1449	1751
$\nu_{asym.}(SO_2)$ $\nu_{sym.}(SO_2)$	1317	968	877	1234	1626
ν(SN)	1144	761	709	1048	1375
π(CH)	897	900	990	866	1035
	837	857	848	752	925
Sulfadimethoxine					
$\nu_{asym.}(NH_2)$aniline	3447	3303	3236	3699	3499
$\nu_{sym.}(NH_2)$aniline	3345	3359	3156	3611	3418
ν(NH)sulfonamide	3226	3275	3213	3661	3454
$\delta(NH_2)$	1651	1718	1514	1449	1751
$\delta(CH_3)$	1438	1483	1398	1354	1544
$\delta(CH_3)$	1352	1475	1368	1348	1542
$\nu_{asym.}(SO_2)$	1314	991	889	1229	1595
	1271	1427	1271	1227	1474
ν(C-O)	1196	776	716	1030	1364
$\nu_{sym.}(SO_2)$	879	922	972	829	1021
ν(SN)					
Sulfamethoxazole					
$\nu_{asym.}(NH_2)$aniline	3462	3304	3236	3699	3500
$\nu_{sym.}(NH_2)$aniline	3376	3259	3157	3610	3419
ν(NH)sulfonamide	3292	3288	3226	3664	3462
$\nu_{asym.}(SO_2)\nu_{sym.}(SO_2)$	1317	991	895	1287	1366
ν(SN)	1157	804	701	1050	–[a]
π(CH)	929	927	989	853	1020
	828	858	854	757	926

[a] Not identified in the calculated spectrum.

considered as a rather high value. The correlation coefficients are affected by the points corresponding to SO_2 stretching vibrations of sulfonamides, whereas for AM1 and PM3 methods strongly underestimate them. In our previous studies, $\nu_{asym.}(SO_2)$ and $\nu_{sym.}(SO_2)$ had been observed at 1317 cm^{-1} and 1144 cm^{-1} for SD[3]; 1314 cm^{-1} and 1196 cm^{-1} for SDMX[1]; 1317 cm^{-1} and 1157 cm^{-1} for SMX[2], respectively. As seen from Table 1, the big

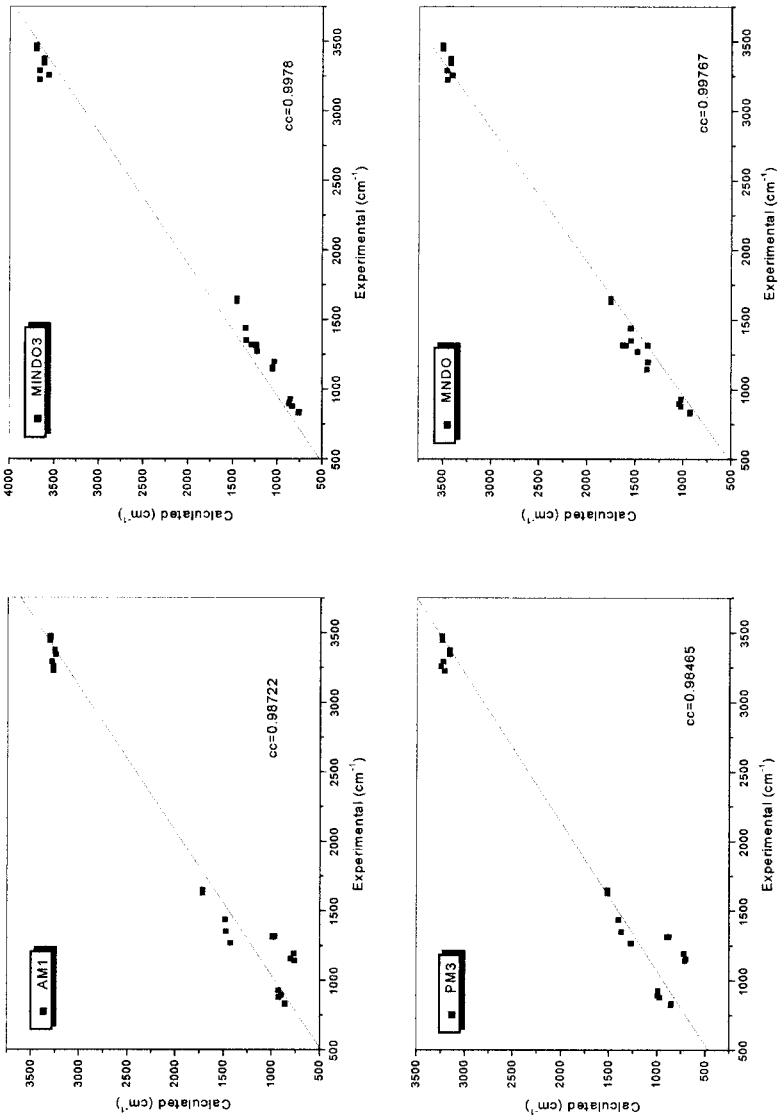

Figure 5. Graphic correlation between the experimental and calculated wave numbers obtained by the methods PM3, AM1, MNDO, and MINDO3 for sulfonamides; cc, correlation coefficient.

underestimation's (almost 25% and 33% for AM1 and 32% and 39% for PM3) have been found for these vibrations. Such underestimation's do not exceed 10% for the MINDO3 method. The wave number values of SO_2 stretching vibrations are overestimated by MNDO by less than 17%. The bigger overestimation (almost 33% for PM3 and up to 39% for MINDO3) had been reported for ring breathing vibration in cycloproply cyanide and not explained[12].

Scaling the simulated spectra had not been neglected by other researchers[4,12,13]. The scaling factors for the wave numbers of N-3-pyridinylmethanesulfonamide and some nitriles were taken in the range 0.82–1.02[4] and 0.84–0.95[12,13], respectively. In our study, the scaling factors for the whole spectral range are equal 1.

The graphical correlations for band intensities can be obtained similar to those given for the wave numbers in Fig. 5. However, it is known that none of semi-empirical methods is able to predict infrared intensities and a spectral intensity pattern. In our study, an attempt to obtain graphical correlations for them also gave absolutely random distributions so we paid more attention to the band positions rather than to band intensities.

In conclusion, IR spectra simulated by the semi-empirical method MINDO3 presents the best match to the observed spectra and also this method provides the best linearity between calculated and experimental wave numbers (correlation coefficient of 0.99780). The assignments of the individual vibrations were confirmed by animation option of the HYPERCHEM programme which gave a visual presentation of the shape of the vibrational modes.

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