

NORMAL COORDINATE ANALYSIS OF SULPHAMIDE

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ABSTRACT

A normal coordinate analysis of sulphamide $\text{SO}_2(\text{NH}_2)_2$ molecule is carried out using the 'characteristic set of valence coordinates' introduced by Herranz and Castano¹ and a set of potential energy constants is reported. Mean vibrational amplitudes, coriolis constants and thermodynamic quantities for a harmonic oscillator approximation, at different temperatures are also evaluated.

INTRODUCTION

THE study of sulphamide is of general interest because of its marked acid properties and its ability to form salts of the type $\text{SO}_2(\text{NHAg})_2$. The exact nature of the force field of a molecule cannot be determined unambiguously from the vibrational frequencies alone. To fix the force fields completely, additional data like mean vibrational amplitudes, coriolis constants and thermodynamic properties are often necessary. However, approximate force fields can be determined using the kinematic method suggested by Herranz and Castano¹. The present paper deals with the analysis of molecular force fields of the sulphamide molecule using the above method.

1. POTENTIAL ENERGY CONSTANTS

The molecule sulphamide belongs to C_{2v} point group nearly in agreement with X-ray results² and with the fundamental vibrational frequencies² falling under the irreducible representation $\tau = 4a_1 + 1a_2 + 2b_1 + 2b_2$. From the vibrational frequencies² and structural parameters³ of this molecule, the symmetry coordinates and the corresponding inverse kinetic energy G matrix elements were constructed. The potential energy F matrix elements were obtained by Herranz and Castano method¹.

$$L^{-1} = \mathbf{B} \mathbf{M}^* \mathbf{B}^*$$

where B is the orthogonal matrix which diagonalises G. M is a diagonal matrix whose elements are the reciprocals of the eigenvalues of G. The asterisk refers to the transpose. The symmetry force constant matrix is given by

$$\mathbf{F} = \mathbf{L}^{-1} \mathbf{*} \mathbf{\Omega} \mathbf{L}^{-1}$$

where $\mathbf{\Omega}$ is a diagonal matrix with

$$\Omega_k = 4\pi^2 c^2 \gamma_k^2.$$

γ_k is the k th frequency (cm^{-1}) and c is the velocity of light (cm/sec). The symmetry coordinates in the present work are essentially the same as those of Ramaswamy and Jayaraman⁴ where the constants a , b , c and d have the

following values : $a = 0.852099$, $b = 0.977023$, $c = 0.420161$, and $d = 1$.

Also $\mathbf{D} = \text{S} - \text{O}$, $\mathbf{d} = \text{S} - (\text{NH}_2)$, $\alpha = \text{O}\hat{\text{S}}\text{O}$
 $\beta = (\text{NH}_2) - \hat{\text{S}} - (\text{NH}_2)$ and $\gamma = (\text{NH}_2) - \bar{\text{S}} - \text{O}$.

The valence force constants thus evaluated are presented in Table I.

TABLE I

Valence force constants of sulphamide molecule

| Bond stretching and bond-bond interactions* | | Bond angle interactions** | | Angle-angle interactions† | |
|---|----------|---------------------------|---------|---------------------------|--------|
| f_D | 12.1114† | $f_{D\alpha}$ | 1.8276 | f_α | 1.3747 |
| f_d | 6.3103 | $f_{d\beta}$ | 1.1146 | f_β | 1.9960 |
| f_{DD} | -0.3556 | $f_{D\gamma}$ | -2.4984 | f_γ | 1.5920 |
| f_{dd} | 0.4780 | $f_{d\gamma}$ | 1.3237 | | |
| f_{Dd} | 0.5434 | | | | |

* in m.dynes \AA^{-1} ; ** in m.dynes rad^{-1} ;

† in m.dynes $\text{\AA}^{-1} \text{rad}^{-2}$;

‡ This number of significant figures is retained for internal consistency in the calculations.

2. MEAN AMPLITUDE OF VIBRATIONS

The important vibrational mean amplitudes of different bonds were calculated by the method of Cyvin⁵ and the nonbonded ones by the method of Ramaswamy *et al.*⁶ and are presented in Table II.

TABLE II

Mean vibrational amplitudes of sulphamide $\text{SO}_2(\text{NH}_2)_2$ molecule of XO_2Y_2 type

| | |
|--------|----------------------|
| X = O | 0.03690 \AA |
| X — Y | 0.04400 |
| Y .. Y | 0.05936 |
| O .. Y | 0.06488 |
| O .. O | 0.05548 |

(Dotted line represents nonbonded distance)

3. CORIOLIS COUPLING CONSTANTS

The coriolis coupling constants (ζ) were evaluated using the relation given by Meal and Polo⁷ and are presented in Table III.

TABLE III
Coriolis coupling coefficients of sulphamide

| coupling species | ζ_{ij}^x | coupling species | ζ_{ij}^y | coupling species | ζ_{ij}^z |
|------------------|--|------------------|--|------------------|--|
| $a_1 \times b_2$ | ζ_{18}^x 0.0055 ζ_{28}^x 0.0077 ζ_{38}^x 0.7421 ζ_{48}^x -0.6371 ζ_{19}^x 0.4618 ζ_{29}^x -0.4408 ζ_{39}^x -0.4914 ζ_{40}^x -0.5982 | $a_1 \times b_1$ | ζ_{16}^y 0.0182 ζ_{26}^y 0.0196 ζ_{36}^y 0.6599 ζ_{46}^y 0.7559 ζ_{17}^y 0.6920 ζ_{27}^y -0.4744 ζ_{37}^y -0.4711 ζ_{47}^y 0.5682 | $a_1 \times a_2$ | ζ_{16}^z 0.6408 ζ_{26}^z -0.5546 ζ_{36}^z 0.5309 ζ_{46}^z 0.0785 |
| $a_2 \times b_1$ | ζ_{56}^x -0.1929 ζ_{57}^x -0.2412 | $a_2 \times b_2$ | ζ_{58}^y 0.1803 ζ_{59}^y 0.1252 | $b_2 \times b_2$ | ζ_{68}^z -0.0023 ζ_{69}^z 0.8000 ζ_{78}^z 0.6956 ζ_{79}^z -0.4362 |

TABLE IV
Thermodynamic properties of sulphamide molecule

| T° K | $(H^\circ - E_0)/T^*$ | $-(F^\circ - E_0)/T^*$ | S° | C_p° |
|---------|-----------------------|------------------------|-----------|-------------|
| 100° | 8.0398 | 48.1875 | 56.2273 | 8.4992 |
| 200° | 9.1192 | 54.0297 | 63.1469 | 12.1276 |
| 298.16° | 10.7032 | 57.9618 | 68.6650 | 15.6004 |
| 300° | 10.7334 | 58.0277 | 68.7611 | 15.6571 |
| 400° | 12.3106 | 61.3351 | 73.6457 | 18.2827 |
| 500° | 13.7024 | 64.2354 | 77.9378 | 20.1477 |
| 600° | 14.8925 | 66.8418 | 81.7343 | 21.4626 |
| 700° | 15.9017 | 69.2154 | 85.1171 | 22.3999 |
| 800° | 16.7587 | 71.3963 | 88.1549 | 23.0807 |
| 900° | 17.4905 | 73.4135 | 90.9040 | 23.5857 |
| 1000° | 18.1200 | 75.2897 | 93.4097 | 23.9681 |

H° = heat content, F° = free energy, S° = Entropy, C_p° = heat capacity, E_0 = Energy per gm. mol of the perfect gas at $T = 0^\circ$ Cal deg⁻¹ mol⁻¹.

4. THERMODYNAMIC PROPERTIES OF SULPHAMIDE

A set of thermodynamic quantities is also calculated and presented in Table IV.

Principal moments of inertia calculated are

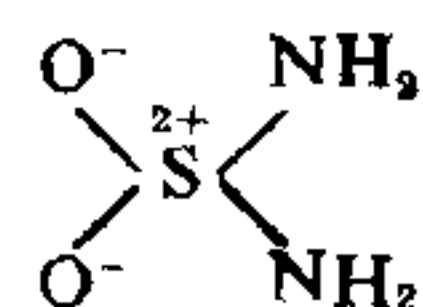
$$I_{xx} = 97.4299 \text{ a.m.u.}\text{\AA}^2, \quad I_{yy} = 87.0582 \text{ a.m.u.}\text{\AA}^2, \\ I_{zz} = 102.2358 \text{ a.m.u.}\text{\AA}^2.$$

RESULTS AND DISCUSSION

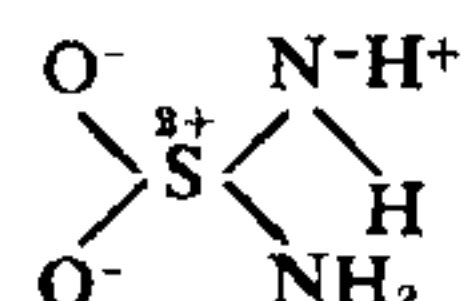
In these calculations, the approximation that the (NH₂) group is a point mass, has been made. The mean amplitude value for nonbonded distance O...O (0.05548 Å) agrees favourably with others^{8,9} for similar types of molecules. The reliability of the ζ (zeta) of Table III is confirmed since they obey the following sum rules.

$$\begin{aligned} (\zeta_{18}^x)^2 + (\zeta_{28}^x)^2 + (\zeta_{38}^x)^2 + (\zeta_{48}^x)^2 &= 1 \\ (\zeta_{19}^x)^2 + (\zeta_{29}^x)^2 + (\zeta_{39}^x)^2 + (\zeta_{40}^x)^2 &= 1 \\ (\zeta_{16}^y)^2 + (\zeta_{26}^y)^2 + (\zeta_{36}^y)^2 + (\zeta_{46}^y)^2 &= 1 \\ (\zeta_{16}^z)^2 + (\zeta_{26}^z)^2 + (\zeta_{36}^z)^2 + (\zeta_{46}^z)^2 &= 1 \end{aligned}$$

At present no experimental data are available to check the calculations of coriolis constants, mean amplitudes and thermodynamic properties reported in this paper. From the bond order calculation¹⁰ [S-O (2.2), S-N (1.7)] supporting the resonance structure, the valence bond structure may be written



In each >N-H bond there may be resonance between the covalent and the ionic >N⁻H⁺ states and the formation of negative charge on the nitrogen atom increases the stability of the molecule in view of the gain of electrostatic energy in the S-N bond. Thus the contribution of the structure



may be large in view of the increased stability produced by the alternative positive and negative charges. The marked acid properties of sulphamide and its ability to form salts of the type $\text{SO}_2(\text{NHAg})_2$ may be in agreement with this structure.

The authors express their thanks to Dr. K. N. Kuchela and to Prof. M. A. Venkatachar for their interest in this work.

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NEUTRAL COMPONENTS OF *THESPESIA POPULNEA* FLOWERS

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ABSTRACT

The flowers of *Thespesia populnea* have been found to contain nonacosane, lupenone, myricyl alcohol, lupeol, β -sitosterol and β -sitosterol- β -D-glucoside.

THE flowers of *Thespesia populnea* have been investigated a number of times in the past, with reference to the polyphenolic components present¹⁻³. When the material is extracted in succession with petroleum ether (60–80°), acetone and alcohol, the flavonoids as aglycones and glycosides are found largely in the alcoholic extract⁴. The petroleum ether extract has yielded (+) gossypol as the main component⁵. The present note gives particulars of neutral components now isolated.

The flowers of *Thespesia populnea* (3 kg) were exhaustively extracted with petroleum ether (60–80°) and the extract deposited the yellow pigment (+) gossypol, reported earlier by Datta *et al.*⁵. The petroleum ether was completely removed and the residue taken up in ether. It was extracted with sodium hydroxide. Acidification of the alkaline extract gave a little more of (+) gossypol. On evaporation of the remaining ether extract a dark coloured semi-solid was obtained. It was adsorbed on silica gel and chromatographed on a column of the same whereby the following compounds were obtained.

Compound A, eluted with petroleum ether, had m.p. 64–65° (300 mg, from acetone). Its I.R. spectrum showed that it was aliphatic in nature. It did not answer Liebermann-Burchard test and moved to solvent front on TLC in *n*-hexane. Its mass-spectrum showed a very weak parent peak at *m/e* 408 and showed a cluster of peaks 14 units ($-\text{CH}_2$) apart. The largest peak in each cluster represented $\text{C}_n\text{H}_{2n+1}$ fragment which was accompanied by C_nH_{2n} and $\text{C}_n\text{H}_{2n-1}$ peaks. Very

intense peaks were for C-4 and C-5 units and the fragment intensity decreased in a smooth curve up to $(\text{M}^+-\text{C}_2\text{H}_5)$. The (M^+-CH_3) peak was very small. The compound was identified as nonacosane.

Compound B, eluted with petroleum ether-benzene (1 : 1), had m.p. 168–170° (from acetone, 40 mg), $[\alpha]_D - 40^\circ$; ν_{max} 1725 cm^{-1} (C=O) and gave a phenyl hydrazone, m.p. above 300°. Liebermann-Burchard test was positive. The compound was identified as lupenone.

Compound C, eluted with benzene, had m.p. 80° (from acetone, 200 mg), ν_{max} 3500 cm^{-1} (OH) and gave an acetate, m.p. 67–69°. The mass-spectrum of the acetate showed the parent peak at *m/e* 480 and the base peak at 421, confirming the presence of the acetate group (M^+-59). It also showed a cluster of peaks 14 units ($-\text{CH}_2$) apart. Very intense peaks were for C-6, C-7 and C-8 units. The compound was identified as myricyl alcohol.

Compound D, eluted with benzene : chloroform (3 : 1), had m.p. 218° (from methanol, 80 mg), $[\alpha]_D + 20^\circ$; ν_{max} 3500 cm^{-1} (OH). It formed an acetate, m.p. 215°. $[\alpha]_D + 50^\circ$. Liebermann-Burchard test was positive. The compound was identified as lupeol.

Compound E, eluted with benzene : chloroform (1 : 3), had m.p. 136–137° (from methanol, 200 mg), $[\alpha]_D - 40^\circ$, ν_{max} 3500 cm^{-1} (OH) and gave an acetate, m.p. 125–126° (from methanol), $[\alpha]_D - 35^\circ$. Liebermann-Burchard and TNM tests were positive. The compound was identified as β -sitosterol.

Compound F, eluted with chloroform : methanol (95 : 5), did not melt up to 300° and was not