Mean Amplitudes of Vibration and the Linear Shrinkage Effect in Sulphur Dicyanide

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Pierce *et al.*[1] have recently carried out a normal-coordinate analysis of the vibrations of sulphur dicyanide, making it possible to compute the mean amplitudes of vibration [2] for this compound. The mentioned workers [1] also demonstrated the linearity of SCN chains to be present, at least to a high degree of accuracy. For this reason the molecule has particular interest because of the linear Bastiansen-Morino shrinkage effect,[3] which is accessible from the harmonic-vibrations analysis.

The present computations were based on the bent symmetrical $S(CN)_2$ model with linear SCN chains; symmetry C_{2v}. One used an initial force field with six force constants from Pierce *et al.*[1] These force constants were adjusted to fit accurately the observed vibrational frequencies,[1] whereby more nonvanishing interaction force constants were introduced. It is not the intention to specify here the final force field used in the present calculations. Table 1 shows the calculated mean amplitudes of vibration. The interatomic distances used as equilibrium values are shown in parentheses for each atom pair. The table also includes the results for the linear Bastiansen-Morino shrinkage effect. The quantities are given at the temperatures of absolute zero and 298°K.

Table 1. Mean amplitudes of vibration (u), and linear shrinkage effect (δ) for sulphur dicyanide; Å units.

Quantity		$T = 0$	298°K
u(S−C)	(1.701)	0.0439	0.0455
u(C≡N)	(1.156)	0.0349	0.0349
u(SN)	(2.857)	0.0465	0.0484
u(CC)	(2.574)	0.0767	0.0987
u(CN)	(3.531)	0.0861	0.1260
u(NN)	(4.323)	0.1049	0.1810
δ(SN)		0.00776	0.01160

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Oxidative Conversion of 3-Methoxy-4-hydroxyphenyl (Vanyl)* Compounds to Fluorescent Substances

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Recently, two independent methods for the quantitative determination of homovanillic acid (3-methoxy-4-hydroxyphenylacetic acid or vanylacetic acid, VAA) have been developed, based upon a strong blue fluorescence emitted after oxidation of the acid. In the method of Sharman [1] VAA is oxidized with ferric chloride in an acid medium with subsequent alkalinization, whereas Andén, Roos and Werdinius [2] employ potassium ferricyanide as oxidant in an alkaline medium. The fluorescent compound has been isolated, and its chemical structure established as 2,2′-dihydroxy-3,3′-dimethoxy-biphenyl-5,5′-diacetic acid.[3]

However, neither of these methods is specific for VAA. A fluorescence of the same nature is exhibited by vanylethylamine (VEA), vanylacetamide, some vanyl-α-alkylacetic acids and their amides,[3] as well

* See Gjessing [9] for a proposed nomenclature of aromatic amino acid metabolites.

as β-vanylpropionic acid (dihydroferulic acid). Since VAA as a metabolite of dopamine is present in urine [4] and brain tissue,[1,2] it would be of interest to determine if other related substances possibly present in biological tissue would give the same type of fluorescence after oxidation.

Vanyllactic acid (VLA) is present in urine from patients with neuroblastoma [5] and in the urine from dogs.[6] Further, it might be present in brain, as aromatic amino acid transaminases have been found in this tissue.[7]

Upon examination both VAA and VLA, as well as the other compounds mentioned, were found to give a blue fluorescence of nearly the same intensity, when 1 ml of an aqueous solution (1 — 10 μg substance) were treated with 5 N ammonia (1 ml), 0.01 % potassium ferricyanide (0.2 ml) and, after 4 min, with 0.1 % cysteine (0.2 ml). The fluorescence was read in an Aminco-Bowman spectrophotofluorometer, with the activation and fluorescence wavelengths set at 315 and 425 mμ, respectively (uncorrected instrumental values).

Since vanyl compounds with both alkaline (VEA), neutral (vanylacetamides), and acidic (VAA, VLA, β-vanylpropionic acid) side chains emit this blue fluorescence upon oxidation, some other compounds of similar nature were also studied. Vanylethanol (VE) and vanylalanine (Van) also reacted with the formation of the blue fluorescence to the same extent as VAA, whereas vanylglycolic acid (3-methoxy-4-hydroxymandelic acid), β-vanylacrylic acid (ferulic acid), vanylformic acid (vanillic acid), and vanillin did not. Vanyl-α-methoxyacetic acid gave a weak fluorescence intensity, about 15 % compared to that of VAA.

The structure necessary for this fluorescence reaction therefore seems to be a vanyl group with a side chain containing at least two carbon atoms and beginning with a methylene group, *i.e.* 3,4-(CH_3O)-$(OH)C_6H_3CH_2C \equiv$. Substances with this structure (*e.g.* VAA, vanylacetamides, VEA, VLA, VE, Van, and β-vanylpropionic acid) also all gave a similar blue colour with diazotized *p*-nitroaniline on paper chromatograms. This colour reaction seems to be specific for the same vanylmethylene structure.[8] The methylene group may be substituted with an alkyl group (as in α-propyl-VAA [3]), but not with a hydroxyl group (as in vanylglycolic acid: no fluorescence reaction, violet colour reaction). An alkoxy group reduces the fluorescence intensity considerably, as in vanyl-α-methoxyacetic acid (blue-violet colour reaction).

Salicylic acid causes serious interference with the oxidation procedure for VAA, as it turns fluorescent in alkaline medium, with maximal activation and fluorescence wavelengths of 295 and 410 mμ, respectively. These wavelengths are close to the maxima obtained from oxidized VAA. On the other hand, salicylic acid gives a colour with diazotized *p*-nitroaniline which is red and very different from that given by VAA.

Methods for the quantitative determination of vanyl compounds, such as vanylethanol and vanylalanine, might be developed on the basis of the fluorescence reaction described, provided that the compounds could be properly separated. For this purpose bidimensional paper chromatography might be employed.[8]

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