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Intramolecular Force Field of Tetrazine Molecule

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An orthonormalised set of symmetry coordinates, satisfying the transformation properties has been constructed for s-tetrazine molecule. With the help of Wilson's FG matrix method and using the molecular kinetic constants, a set of potential constants have been obtained. The other constants, namely, compliance constants, mean amplitudes of vibration, Coriolis coupling constants and centrifugal distortion constants have also been evaluated for the first time in the present work.

INTRODUCTION

The *s*-tetrazine molecule offers itself a very good example for the application of group theory and understanding the nature of molecular vibrations. Many researchers have reported the vibrational analysis of the molecule, *s*-tetrazine. The first group of investigators[1] restrict their analysis of the spectrum in the region 700–4000 cm^{-1} due to the inefficiency of the Raman spectrophotometers for coloured samples like tetrazine. By using a helium-neon laser source in the spectrophotometer, Franks *et al*[2] reported the Raman spectrum. Sigworth *et al*[3] investigated the low temperature IR and Raman spectra of thin films of the three forms of tetrazine (liquid, solid and vapour) and they performed a normal coordinate analysis for the in-plane vibrations. The assignments made by Sigworth *et al*[3] were tested by Kawaguchi *et al*[4] using a modified Urey Bradley force field. The problem relating to the normal coordinate analysis of *s*-tetrazine still contains further possibilities of improvement. The present paper is devoted to a thorough discussion of the problem on the basis of most general quadratic valence force field and the utilisation of molecular kinetic constants. The other molecular constants such as the compliance constants, vibrational mean amplitudes, Coriolis coupling constants and centrifugal distortion constants have also been evaluated and they are presented here for the first time.

THEORETICAL CONSIDERATIONS

The molecule *s*-tetrazine belongs to D_{2h} symmetry having 18 fundamental frequencies out of which 13 in-plane vibrations are active in both IR and Raman spectra. They are distributed as

$$\Gamma = 4A_g + 3B_{3g} + 3B_{1u} + 3B_{2u}$$

The remaining frequencies, distributed in the following species,

$$\Gamma = 2B_{2g} + 1A_u + 2B_{3u}$$

constitute the out of plane modes. Since there is no interaction between these two sets of motion, the in-plane vibrations alone are taken in this paper to determine the potential constants. The structure and nomenclature of the parameters of *s*-tetrazine are shown in Figure 1. The symmetry coordinates formed in the present work subject to the well known group, theoretical considerations are given below

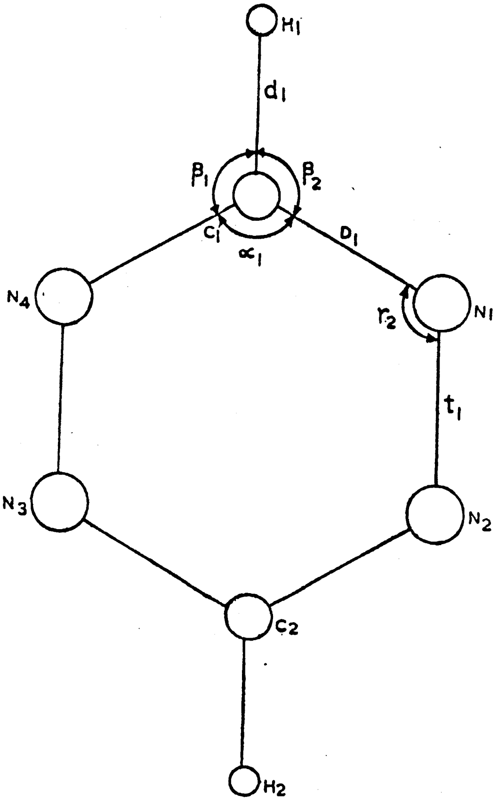

Fig. 1 Structure and nomenclature of the parameters of *s*-tetrazine

A_g species :

$$S_1 = \frac{1}{\sqrt{2}} (\Delta d_1 + \Delta d_2)$$

$$S_2 = \tfrac{1}{2}(\Delta D_1 + \Delta D_2 + \Delta D_3 + \Delta D_4)$$

$$S_3 = \frac{1}{\sqrt{2}} (\Delta t_1 + \Delta t_2)$$

$$S_4 = \frac{D}{\sqrt{2}} (\Delta \alpha_1 + \Delta \alpha_4)$$

B_{3g} species :

$$S_5 = \tfrac{1}{2}(\Delta D_1 - \Delta D_2 + \Delta D_3 - \Delta D_4)$$

$$S_6 = \frac{\sqrt{dD}}{2}(\Delta\beta_1 - \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4)$$

$$S_7 = \frac{\sqrt{tD}}{2}(\Delta\gamma_2 - \Delta\gamma_3 + \Delta\gamma_5 - \Delta\gamma_6)$$

B_{1u} species :

$$S_8 = \frac{1}{\sqrt{2}}(\Delta d_1 - \Delta d_2)$$

$$S_9 = \tfrac{1}{2}(\Delta D_1 - \Delta D_2 - \Delta D_3 + \Delta D_4)$$

$$S_{10} = \frac{D}{\sqrt{2}}(\Delta\alpha_1 - \Delta\alpha_4)$$

B_{2u} species :

$$S_{11} = \tfrac{1}{2}(\Delta D_1 + \Delta D_2 - \Delta D_3 - \Delta D_4)$$

$$S_{12} = \frac{1}{\sqrt{2}}(\Delta t_1 - \Delta t_2)$$

$$S_{13} = \frac{\sqrt{tD}}{2}(\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 + \Delta\beta_4)$$

where Δd, ΔD and Δt are the changes in C—H, C—N and N—N bond distances respectively, $\Delta\alpha$, $\Delta\beta$ and $\Delta\gamma$ are the change, in $N\hat{C}N$, $N\hat{C}H$ and $C\hat{N}N$ interbond angles.

The most general quadratic potential energy function has been constructed for *s*-tetrazine and making use of the expression $F = uf\tilde{u}$, the F-matrix elements have been evaluated, and are given below:

A_g Species :

$$F_{11} = f_d + f_{dd}$$

$$F_{22} = f_D + (f_{DD})_1 + (f_{DD})_2 + (f_{DD})_3$$

$$F_{33} = f_t + f_{tt}$$

$$F_{44} = f_\alpha + f_{\alpha\alpha}$$

$$F_{12} = \sqrt{2}(f'_{dD} + f''_{dD})$$

$$F_{13} = 2(f_{dt})$$

$$F_{14} = f'_{d\alpha} + f''_{d\alpha}$$

$$F_{23} = \sqrt{2}(f'_{dD} + f''_{dD})$$

$$F_{24} = \sqrt{2}(f'_{D\alpha} + f''_{D\alpha})$$

$$F_{34} = 2f_{t\alpha}$$

B_{3g} *Species* :

$$F_{55} = f_D + (f_{DD})_1 - (f_{DD})_2 + (f_{DD})_3$$
$$F_{66} = f_\beta + f''_{\beta\beta}$$
$$F_{77} = f_\gamma - f''_{\gamma\gamma}$$
$$F_{56} = 0$$
$$F_{57} = (f_{D\gamma})_1 + (f_{D\gamma})_3 - 2(f_{D\gamma})_2$$
$$F_{67} = 0$$

B_{1u} *Species* :

$$F_{88} = f_d - f_{dd}$$
$$F_{99} = (f_D) + (f_{DD})_3 - (f_{DD})_1 - (f_{DD})_2$$
$$F_{10,10} = f_\alpha - f_{\alpha\alpha}$$
$$F_{89} = 2(f''_{dD} - f'_{dD})$$
$$F_{8,10} = f''_{d\alpha} - f'_{d\alpha}$$
$$F_{9,10} = \sqrt{2}(f''_D - f_D)$$

B_{2u} *Species* :

$$F_{11,11} = f_D + (f_{DD})_2 - (f_{DD})_1 - (f_{DD})_3$$
$$F_{12,12} = f_t - f_{tt}$$
$$F_{13,13} = f_\beta - f''_{\beta\beta}$$
$$F_{11,12} = \sqrt{}(f''_{Dt} - f'_{Dt})$$
$$F_{11,13} = 0$$
$$F_{12,13} = \sqrt{2}(f'_{t\beta} - f''_{t\beta})$$

From a knowledge of Wilson's kinetic energy expression $2T=\tilde{\dot{S}}G^{-1}\dot{S}$, the kinetic constants are evaluated. By the method of kinetic constants[5–7] the secular equations relating to the potential constants are solved. The compliance constants for this molecule have been evaluated by the method of Decius[8]. The vibrational mean amplitude quantities have been evaluated at 298.16 K for both the bonded and non-bonded atoms using Cyvin's relation.[9,10]

A set of potential constants are useful in evaluating the Corfolis coupling constants theoretically which are used for the interpretation of spectra. John's rule[11] is made use of to find the couplings which are effective in this molecule. They are

$$A_g \times B_{3g}(\text{X-axis}) \quad \text{and} \quad B_{1u} \times B_{2u}(\text{X-axis})$$

The zeta matrix elements are evaluated from the matrix relation $\zeta^{\alpha} = L^{-1}C^{\alpha}\tilde{L}^{-1}$ where L is the normal coordinate transformation matrix and C^{α} is the Coriolis matrix obtained by the vector method of Meal and Polo[12].

Cyvin *et al.*[9, 10] have reformulated the theory of rotational distortion by introducing certain new elements $J_{\alpha\beta}$'s instead of partial derivatives of inertia tensor components $J_{\alpha\beta}$'s of Kivelson[13] and Wilson[14]. The quantities $t_{\alpha\beta\gamma\delta}$ have been obtained using Cyvin's relation[9, 10]; hence centrifugal distortion constants have been evaluated.

RESULTS AND DISCUSSION

The molecular parameters and vibrational frequencies employed in the present investigation are given in Table 1. Table 2 reports the kinetic constants, potential constants and compliance constants of *s*-tetrazine. A comparison of some of the potential constants with the earlier works is given in Table 3. From these tables the following facts are observed.

TABLE 1

MOLECULAR PARAMETERS AND VIBRATIONAL FREQUENCIES OF *s*-TETRAZINE

Molecular Parameters	Frequencies			Frequencies		
	Obs.	cm^{-1}	Cal.	Obs.	cm^{-1}	Cal.
d(C—H) 1.084 A	$\nu_1(A_g)$	3088.5	3085.0	$\nu_8(B_{1u})$	3085.5	3082.5
D(C—N) 1.334 A	$\nu_2(A_g)$	1416.5	1420.5	$\nu_9(B_{1u})$	1203.5	1200.0
t(N—N) 1.321 A	$\nu_3(A_g)$	1015.0	1014.0	$\nu_{10}(B_{1u})$	1093.0	1088.0
$\alpha = 127.37°$	$\nu_4(A_g)$	734.0	732.0	$\nu_{11}(B_{2u})$	1109.0	1108.5
$\beta = 116.315°$	$\nu_5(B_{3g})$	1522.5	1524.0	$\nu_{12}(B_{2u})$	893.0	890.0
	$\nu_6(B_{3g})$	649.0	653.0	$\nu_{13}(B_{2u})$	1447.5	1446.5
	$\nu_7(B_{3g})$	1302.0	1306.5			

(1) The kinetic constants of the bonds which form the ring (k_D and k_t) are higher than that of the C–H bond (k_d).

(2) Almost all the bond-angle interaction kinetic constants are negative.

(3) Considering the potential constants, the C–H bond stretching potential constant f_d is in good agreement with that obtained for benzene and also with those obtained for s-tetrazine by Sigworth *et al.*[3] and Kawaguchi *et al.*[4]

(4) The earlier investigators have reported 6.168 and 6.6 respectively for f_D. The value for the same bond stretching force obtained in the present work is 7.5127. This is reasonable because of the

TABLE 2

KINETIC (k), POTENTIAL (f) AND COMPLIANCE (n) CONSTANTS OF *s*-TETRAZINE

	k (10^{-29} kg)	f (10^2 N/m)	n (10^{-2} n/N)
d	0.1845	5.2816	0.1035
D	2.9159	7.5127	0.5302
t	3.4625	6.9854	0.5501
dd	0.0213	0.4085	−0.0117
dD′	0.1985	0.6112	−0.0118
dD″	0.2238	0.4075	−0.0023
dt	0.2379	0.5091	0.0078
$(DD)_1$	1.4142	2.5663	−0.3951
$(DD)_2$	1.2474	−0.3117	0.3608
$(DD)_3$	1.7586	1.6425	−0.3985
Dt′	1.7835	−0.3858	0.3969
Dt″	2.0408	2.1012	−0.4152
tt	2.1460	1.8602	−0.4269
α	2.4338	1.9120	0.7404
$d\alpha'$	−0.1806	0.2175	−0.0091
$d\alpha''$	−0.2489	−0.2108	0.0123
$D\alpha'$	−1.8460	−0.4051	0.0149
$D\alpha''$	−1.4235	0.6967	−0.0495
$t\alpha$	−2.0468	−0.1273	0.0221
$\alpha\alpha$	2.5001	−0.9502	0.3411
β	0.0971	1.0926	1827.699
$\beta\beta''$	−0.0058	−1.0926	1826.9891
$t\beta' \Rightarrow t\beta''$	−0.0595	−0.1932	0.0881
$\gamma\gamma \Rightarrow \gamma''$	0.8766	0.6381	0.0025
$(D\gamma)_1 \Rightarrow 2(D\gamma)_2$	0.6206	1.8619	−0.0174

TABLE 3

COMPARISON OF POTENTIAL CONSTANTS (10^2 N/m)

f	Sigworth's values	Kawaguchi's values	Present work
f_d	5.173	5.3	5.2816
f_D	6.168	6.6	7.5127
f_t	5.475	5.9	6.9854
f_α	1.445	1.4	1.9120
$(f_{DD})_1$	0.349	0.5	2.5660
$(f_{DD})_2$	−0.179	−0.4	−0.3117
f'_{Dt}	—	−0.5	−0.3858
f''_{Dt}	1.189	1.2	2.1012
f''_{dD}	0.318	0.4	0.4075

intermediate bond order of the molecule as in the case of benzene (Mohan *et al.*[15–17]).

(5) Based on the above explanation, the value reported here for N–H bond stretching potential constant f_t is reasonable too.

(6) $(f_{DD})_1$ is predominant over the other interaction constants. This constant is concerned with the parallel C–N bonds. It is similar to the case of $(f_{DD})_1$ in benzene which explains the parallel C–C bond interaction.

(7) The interaction potential constant of a highly delocalised bond molecule tends to take positive value while the localised molecule takes a negative value. All interaction constants evaluated in the present work are not compared with the earlier works as they are not available in the literature.

The compliance constants (n) show an opposite trend to the potential constants. Table 4 represents the mean amplitudes of vibrations of

TABLE 4

BONDED AND NON-BONDED MEAN AMPLITUDES OF VIBRATION AT 298.16 K (10^2 pm) AND CENTRIFUGAL DISTORTION CONSTANTS (MH_3)

1		CDC	
1_d(C—H)	0.7696 (0.783)[a]	D_J	204.0308
1_D(C—N)	0.4624 (0.4747)[b]	D_K	167.0689
1_t(N—N)	0.4853	D_{JK}	−368.2806
1_{q_1}($C_1 \ldots N_2$)	0.4992		
1_{q_2}($C_1 \ldots C_2$)	1.0149		
1_{q_3}($C_1 \ldots H_2$)	1.2894		
1_{q_4}($H_1 \ldots N_1$)	1.3713		
1_{q_5}($H_1 \ldots N_2$)	1.2432		
1_{q_6}($H_1 \ldots H_2$)	1.4123		
1_{q_7}($N_1 \ldots N_4$)	0.7570		
1_{q_8}($N_1 \ldots N_3$)	0.7052		

[a]Kivelson's value; [b]Wilson's value.

both bonded and non-bonded distances of s-tetrazine and also the centrifugal distortion constants. From the table it is seen that 1_d, 1_D and 1_t are in the expected range. Mean amplitudes of vibrations and centrifugal distortion constants have been evaluated for the first time. The centrifugal distortion constants evaluated in the present work are in the expected range. It is interesting to note that D_{JK} takes negative value.

Coriolis coupling constants are also reported for the first time in Table 5. The large magnitudes of $|\zeta x_{16}|$, ζx_{27}, ζx_{47}, $\zeta x_{9,11}$, $\zeta x_{9,12}$, $\zeta x_{10,11}$ and $\zeta x_{10,12}$ constants indicate that the coupling between the concerned species is stronger.

TABLE 5

CORIOLIS COUPLING CONSTANTS OF *s*-TETRAZINE

$(A_g \times B_{3g})^x$		$(B_{1u} \times B_{2u})^x$	
ζx_{15}	−0.2286	$\zeta x_{8,11}$	−0.1304
ζx_{16}	−0.9455	$\zeta x_{8,12}$	0.1867
ζx_{17}	0.0011	$\zeta x_{8,13}$	−0.1126
ζx_{25}	0.5444	$\zeta x_{9,11}$	0.8636
ζx_{26}	−0.0577	$\zeta x_{9,12}$	0.9946
ζx_{27}	−0.6527	$\zeta x_{9,13}$	−0.1253
ζx_{35}	−0.1973	$\zeta x_{10,11}$	−0.8257
ζx_{36}	0.2763	$\zeta x_{10,12}$	0.7621
ζx_{37}	0.3671	$\zeta x_{10,13}$	0.5740
ζx_{45}	−0.0388		
ζx_{46}	−0.1408		
ζx_{47}	−0.9756		

Thus a complete and a systematic vibrational analysis is presented for *s*-tetrazine and the values for the molecular constants are reasonable in justifying the assignment for *s*-tetrazine.

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CORRIGENDUM

Paper entitled "Spectrophotometric studies on cobalt(II) complex of 4-methyl dibenzoylmethane" [*Asian J. Chem.*, Vol. 3, No. 3, 337–339 (1991)]:

On page 337, line 14, substitute $Co(NO_3)_2 \cdot 6H_2O$ instead of $Co(NH_3)_2 \cdot 6H_2O$.