

## Potential Functions of 5-Membered Ring-molecules. II. Normal Coordinate Analysis of the Non-planar Vibrations of 1,3,4-Oxadiazole, 1,2,5-Oxadiazole and 1,2,5-Thiadiazole

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Harmonic potential functions of the non-planar vibrations of 1,3,4-oxadiazole, 1,2,5-oxadiazole, and 1,2,5-thiadiazole have been calculated by using deuterium isotopic frequency data. The results are compared with the potential functions of 1,3,4-thiadiazole, thiophene, and furane.

The normal coordinate analysis of the non-planar vibrations of 1,3,4-thiadiazole (I) has been described in a previous paper.<sup>1</sup> Using the same technique the normal coordinate analysis of 1,3,4-oxadiazole (II), 1,2,5-oxadiazole (III), and 1,2,5-thiadiazole (IV) will be carried out in this work.

The complete assignments of the fundamental vibration frequencies of (II),<sup>2-4</sup> (III),<sup>5,6</sup> and (IV)<sup>7</sup> and their deuterated species are recently made. Sufficient frequency data are, therefore, available to determine the harmonic potential functions of the non-planar vibrations of these molecules.

The geometrical structure of (II),<sup>8</sup> (III),<sup>9</sup> and (IV)<sup>10</sup> to be used in the calculations, are known from previous microwave spectroscopy investigations. It was shown that the molecules are planar. The parent molecules and the dideuterated species, therefore, belong to the  $C_{2v}$  point group and the four non-planar fundamental vibrations may be classified as  $2A_2 + 2B_2$ . The monodeuterated species belong to the  $C_s$  point group and the four non-planar fundamental vibrations may be classified as  $4A''$ .

### CALCULATIONS

An earlier attempt to calculate the harmonic force fields of these molecules was made by Cyvin *et al.*<sup>11</sup> on the base of the frequency data from the parent molecules only. From an initial force field they calculated the normal frequencies, which for some of the molecules fitted rather poor to the observed frequencies. The deviations were from  $-23\%$  to  $+19\%$ . From these approximate force fields they calculated the vibration pictures (the L-matrices), *i.e.* the directions and amplitudes of the atomic motions in the normal vibrations. Keeping the L-matrices fixed they fitted the force constants to the observed frequencies. They determined the 6 constants from 4 data with all the uncertainty that implies.

In this investigation the 6 force constants are determined from 6 independent normal frequencies from the parent molecule and the dideuterated species. The 2 normal frequencies left are not independent because of the product rules. Unfortunately a direct comparison with the results of Cyvin *et al.*<sup>11</sup> is not straightforward because of the different symmetry coordinates used. Also, the assignments of the  $A_2$  vibration frequencies have been changed radically for all of the four molecules in question.

The procedure used for the exact solution of the two-dimensional vibration problem is described in detail in Ref. 1. The two kinds of symmetry coordinates, the CH out-of-plane bending coordinates, **S**, and the ring deformation coordinates, **T**, used in this work are

Table 1. 1,3,4-Oxadiazole and its deuterated species. Assigned and adjusted frequencies ( $\text{cm}^{-1}$ ).

	$\text{C}_2\text{H}_2\text{N}_2\text{O}$		$\text{C}_2\text{HDN}_2\text{O}$		$\text{C}_2\text{D}_2\text{N}_2\text{O}$	
	ass.	adj.	ass.	adj.	ass.	adj.
$\nu_7$	825	825.9	727	726.2	709	709.1
$\nu_8$	653	653.7	646	646.3	585	583.2
$\nu_{14}$	852	851.8	840	840.6	747	747.0
$\nu_{15}$	625	625.4	544	543.6	517	516.8

Table 2. 1,2,5-Oxadiazole and its deuterated species. Assigned and adjusted frequencies ( $\text{cm}^{-1}$ ).

	$\text{C}_2\text{H}_2\text{N}_2\text{O}$		$\text{C}_2\text{HDN}_2\text{O}$		$\text{C}_2\text{D}_2\text{N}_2\text{O}$	
	ass.	adj.	ass.	adj.	ass.	adj.
$\nu_7$	888	887.8	868	868.2	757	757.0
$\nu_8$	641	642.3	631	631.4	552	552.8
$\nu_{14}$	838	838.7	712	711.7	640	639.2
$\nu_{15}$	631	631.4	579	578.4	631	630.2

Table 3. 1,2,5-Thiadiazole and its deuterated species. Assigned and adjusted frequencies ( $\text{cm}^{-1}$ ).

	$\text{C}_2\text{H}_2\text{N}_2\text{S}$		$\text{C}_2\text{HDN}_2\text{S}$		$\text{C}_2\text{D}_2\text{N}_2\text{S}$	
	ass.	adj.	ass.	adj.	ass.	adj.
$\nu_7$	908	908.2	883	883.3	781	780.9
$\nu_8$	612	612.1	558	558.4	519	518.9
$\nu_{14}$	838	838.8	719	718.5	651	650.4
$\nu_{15}$	521	521.5	509	508.5	507	506.5

analogous with those used for (I), and similar to the symmetry coordinates previously used of Orza *et al.* in a normal coordinate analysis of the non-planar vibrations of thiophene (V)<sup>12</sup> and furane (VI).<sup>13</sup> The adjustment of the experimental vibration frequencies is made according to the principles earlier described.<sup>1</sup> The experimental and adjusted vibration frequencies for (II), (III), and (IV) are shown in Tables 1, 2, and 3, respectively. It is thus possible to calculate the three symmetry coordinate force constants,  $F_{\text{SS}}$ ,  $F_{\text{ST}}$ , and  $F_{\text{TT}}$  in the harmonic potential function:

$$2V = F_{\text{SS}}\text{S}^2 + 2F_{\text{ST}}\text{ST} + F_{\text{TT}}\text{T}^2$$

in each of the two symmetry species  $A_2$  and  $B_2$  of each of the molecules (II), (III), and (IV).

Also, it is possible to calculate the valence coordinate force constants of the CH out-of-plane bending vibration of the three molecules:

$$f_{\gamma\gamma} = \frac{1}{2}(F_{\text{SS}(B_2)} + F_{\text{SS}(A_2)}) \text{ and } f_{\gamma\gamma'} = \frac{1}{2}(F_{\text{SS}(B_2)} - F_{\text{SS}(A_2)})$$

Furthermore, one can calculate the interaction constants between the CH-valence coordinates  $\gamma$  and  $\gamma'$  and the ring deformation coordinates  $\text{T}$  in each symmetry species,  $A_2$  and  $B_2$ :

$$f_{\gamma\text{T}} = 2^{-\frac{1}{2}}F_{\text{ST}}$$







The values of these constants are shown in Table 4, which also shows the values of the force constants of (I).<sup>1</sup> For comparison the corresponding values for (V) and (VI), calculated by Orza *et al.*<sup>12,13</sup> are included too. The uncertainties of the values are all from 0.001 to 0.002 mdyn Å/rad<sup>2</sup>.

Unfortunately, there are double solutions in the determinations of the ring deformation constants  $F_{\text{TT}}$ , and the interaction constants  $F_{\text{ST}}$ . Only the CH out-of-plane bending force constants  $F_{\text{SS}}$  are unambiguously determined. This problem is well known, and has recently been treated by Fadini.<sup>14</sup> When expanding the secular determinant, one obtains a first-order equation and a second-order equation. The latter is the cause of the double solution. However, in order to compare the results for all of the six molecules (I)–(VI) we selected (as in Ref. 1), somewhat arbitrarily, but in agreement with Orza *et al.*,<sup>12,13</sup> the set of force constants which yield the most characteristic normal modes, as those with physical significance. That is  $Q_7$  and  $Q_{14}$  are mainly CH out-of-plane bending coordinates and  $Q_8$  and  $Q_{15}$  are mainly ring deformation coordinates as shown of the L-matrices which have been calculated for each set of force constants of each molecule. The physical significant values are given in the upper part of Table 4, and the alternative ones are given in the lower part of the table. As will be seen the choice also gives the most similar force constants for the six molecules in question.

## DISCUSSION

Since the geometry of furane, 1,2,5-oxadiazole, and 1,3,4-oxadiazole are very similar and the same is true for thiophene, 1,2,5-thiadiazole, and 1,3,4-thiadiazole it is possible to compare

Table 4. Non-planar vibration force constants of some five-membered ring molecules. (mdyn Å/rad<sup>2</sup>).

						
	VI <sup>a</sup>	II <sup>b</sup>	III <sup>b</sup>	V <sup>c</sup>	I <sup>d</sup>	IV <sup>b</sup>
$f_{\gamma(\alpha)\gamma(\alpha)}$	0.339	0.384	—	0.339	0.382	—
$f_{\gamma(\alpha)\gamma'(\alpha)}$	0.032	0.017	—	0.046	0.023	—
$f_{\gamma(\beta)\gamma(\beta)}$	0.387	—	0.425	0.395	—	0.426
$f_{\gamma(\beta)\gamma'(\beta)}$	-0.025	—	-0.018	-0.031	—	-0.017
$\overline{F}_{T(A_2)T(A_2)}$	0.523	0.391	0.475	0.440	0.310	0.404
$\overline{F}_{T(B_2)T(B_2)}$	0.420	0.413	0.350	0.443	0.423	0.395
$f_{\gamma(\alpha)T(A_2)} = -f_{\gamma'(\alpha)T(A_2)}$	0.115	0.115	—	0.123	0.120	—
$f_{\gamma(\alpha)T(B_2)} = f_{\gamma'(\alpha)T(B_2)}$	-0.140	-0.139	—	-0.169	-0.160	—
$f_{\gamma(\beta)T(A_2)} = -f_{\gamma'(\beta)T(A_2)}$	-0.193	—	-0.190	-0.179	—	-0.171
$f_{\gamma(\beta)T(B_2)} = f_{\gamma'(\beta)T(B_2)}$	0.078	—	0.085	0.091	—	0.086
Alternative value						
$\overline{F}_{T(A_2)T(A_2)}$	0.987	0.527	0.827	0.945	0.331	0.843
$\overline{F}_{T(B_2)T(B_2)}$	0.673	0.731	0.354	1.132	0.935	0.550
$f_{\gamma(\alpha)T(A_2)} = -f_{\gamma'(\alpha)T(A_2)}$	0.203	0.196	—	0.178	0.135	—
$f_{\gamma(\alpha)T(B_2)} = f_{\gamma'(\alpha)T(B_2)}$	-0.254	-0.288	—	-0.361	-0.360	—
$f_{\gamma(\beta)T(A_2)} = -f_{\gamma'(\beta)T(A_2)}$	0.332	—	0.338	0.367	—	0.355
$f_{\gamma(\beta)T(B_2)} = f_{\gamma'(\beta)T(B_2)}$	0.102	—	0.090	0.235	—	0.198

<sup>a</sup> From Ref. 13. <sup>b</sup> This work. <sup>c</sup> From Ref. 12. <sup>d</sup> From Ref. 1.

the force constants of these molecules. From Table 4 it can be seen that the CH out-of-plane bending force constants are of equal size in the analogous oxygen and sulfur compounds of these five-membered ring molecules. However, it also shows that introducing two N-atoms in the furane or thiophene ring causes an increase of these force constants. Contrarily, introducing the two N-atoms in the furane or thiophene ring causes a decrease of the ring deformation force constants, especially the force constants of the symmetry coordinates that mainly involve torsional motion of a N—N, N—O, or an N—S bond, *i.e.*  $T_{A_2}$  of the 1,3,4-compounds and  $T_{B_2}$  of the 1,2,5-compounds. In other words, it is easier to twist a bond between heteroatoms than a C—C bond in these five-membered heteroatomic ringmolecules.

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