

Harmonic Force Fields for Some Heterocyclic Five-Membered Ring Molecules

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Complete sets of harmonic symmetry force constants have been developed for 1,2,5-thiadiazole, 1,2,5-oxadiazole, 1,2,5-selenadiazole, 1,3,4-thiadiazole, 1,3,4-oxadiazole, thiophene, and furan. The calculations were based on observed vibrational frequencies from literature. Calculated frequencies for the molecules are given, including those of thiophene- d_4 , thiophene-2,5- d_2 , thiophene-3,4- d_2 , furan- d_4 , furan-2,5- d_2 , and furan-3,4- d_2 .

Heterocyclic five-membered ring compounds have attracted the interest of many investigators. Especially during the recent years a number of these compounds have been treated by microwave, infrared, and Raman spectroscopy (for references, see below) to give very reliable structural parameters and vibrational frequencies. Complete vibrational assignments are now available for many of the molecules in question, including several isotopic substituents. This material makes it feasible to perform extensive studies of the harmonic force fields, which is the subject of the present work. It was started with the more limited aim of computing mean amplitudes of vibration¹ for 1,3,4-thiadiazole in connection with an electron diffraction investigation of this molecule conducted by the Oslo group. The work was soon extended to include 1,3,4-oxadiazole, 1,2,5-thia-, oxa-, and selenadiazoles, thiophene, and furan. Some conclusions from preliminary calculations for 1,2,5-thiadiazole are reported in the present work. This particular molecule was chosen rather arbitrarily for that purpose. Also some implications of different choices of internal coordinates in the computations of force constants are pointed out and illustrated with numerical examples for 1,2,5-thiadiazole.

MOLECULAR STRUCTURE AND SYMMETRY CONSIDERATIONS

All the molecules here treated are known to be planar and belong to the C_{2v} symmetry group. Complete sets of symmetry coordinates without redundants are specified elsewhere.² These coordinates are convenient for precise

definitions of force constants when the final force fields are presented. They are, however, not so well suitable when initial force constants are to be estimated. The problems of this kind are discussed in some details in some of the subsequent sections.

The structural parameters used as equilibrium distances and angles in the present calculations were taken from different sources,³⁻⁹ and are collected in Table 1.

Table 1. Adopted structure parameters.

Molecule	Equilibrium distances ^a (Å)				Ref.
	X-N	N-C	C-C	C-H	
1,2,5-Thiadiazole	1.632	1.329	1.413	1.080	3,4
1,2,5-Oxadiazole	1.380	1.300	1.421	1.076	5
1,2,5-Selenadiazole	1.830	1.300	1.456	1.079	6
	X-C	N-C	N-N	C-H	
1,3,4-Thiadiazole	1.721	1.302	1.371	1.077	7
1,3,4-Oxadiazole	1.36	1.30	1.37	1.077	assumed
	X-C	C ₂ -C ₃	C ₃ -C ₄	$\begin{cases} \text{C}_2-\text{H}_2 \\ \text{C}_3-\text{H}_3 \end{cases}$	
Thiophene	1.714	1.370	1.423	$\begin{cases} 1.078 \\ 1.081 \end{cases}$	8
Furan	1.362	1.361	1.431	$\begin{cases} 1.075 \\ 1.077 \end{cases}$	9
Molecule	Equilibrium angles (degrees)			Ref.	
	CCN		CCH		
1,2,5-Thiadiazole	113.8		122	3,4	
1,2,5-Oxadiazole	109		130.2	5	
1,2,5-Selenadiazole	118.5		126.2	6	
	NNC		XCH		
1,3,4-Thiadiazole	112.2		122.5	7	
1,3,4-Oxadiazole	112		116	assumed	
	C ₂ C ₃ C ₄	XC ₂ H ₂	C ₄ C ₃ H ₃		
Thiophene	112.45	119.85	124.27	8	
Furan	106.05	115.92	127.95	9	

^a X=S, O, or N.

OBSERVED VIBRATIONAL FREQUENCIES

Observed frequencies and vibrational assignments were adopted from literature, of which a survey is given in the following. For 1,2,5-selenadiazole the experimental frequencies due to Benedetti and Bertini⁶ were used, along with those for 1,2,5-thiadiazole in accord with the quotation in the same work. The frequencies for 1,2,5-oxadiazole¹⁰ and 1,3,4-thiadiazole¹¹ were taken from Sbrana *et al.*; for 1,3,4-oxadiazole from Christensen *et al.*,^{12,13} and

finally the thiophene¹⁴ and furan¹⁵ frequencies were taken from the extensive works of Rico *et al.*,^{14,15} who have included the spectra of several deuterated compounds in their studies. Christensen *et al.*¹⁶ have confirmed the values of Sbrana *et al.*¹⁰ for 1,2,5-oxadiazole.

For quotations of the actual frequency values the reader should refer to the tables of the subsequent sections.

GENERAL PROCEDURE AND THEORY

The force fields were developed by an iterative procedure employing successive fittings to observed frequencies by means of **L** matrices obtained from the usual secular equation.¹⁷ In the cases of thiophene and furan where the frequencies of several isotopic substituents are available a least-squares fitting procedure employing Jacobi elements was applied; see, *e.g.*, Mills.¹⁸ The present section contains a discussion of the principles for setting up the initial force field, which serves as the starting point of the iteration procedures.

As to the out-of-plane force field one may work with force constants in terms of the simple symmetry coordinates without redundants² throughout the analysis. It is believed that a valence force field (*i.e.* diagonal **F** matrix) may be found which gives a useful starting point for the computations.

In the case of the in-plane force field, however, precaution must be taken when the coordinate set for the planar ring deformations is to be chosen. There is no physical reason for assuming that the **F** matrix in terms of the particular symmetry coordinates of Ref. 2 should be diagonal, since under the construction of these coordinates two somewhat arbitrarily selected, but physically important types of ring bendings were omitted in order to avoid redundants. When these bendings are added to the other in-plane valence coordinates, however, it is supposed that a valence force field may be set up with good confidence.

Let **r** represent the augmented set of valence coordinates, and let **f** designate the corresponding force-constant matrix, which incidently may be chosen as diagonal. When **S** represents the complete symmetry coordinate set without redundants it must be possible to express any coordinate from **r** uniquely in terms of **S**, say

$$\mathbf{r} = \mathbf{T} \mathbf{S} \quad (1)$$

Since the **r** coordinates contain redundants the transformation matrix **T** is rectangular and has no inverse. Nevertheless the matrix **T** may be used to convert the force constants of **f** into the symmetrized form (**F**) according to

$$\mathbf{F} = \mathbf{T}' \mathbf{f} \mathbf{T} \quad (2)$$

where **T'** is the transpose of **T**. This relation cannot be inverted. In other words an **f** matrix cannot be computed uniquely from a given **F**. This feature may also be deduced from the fact that certain combinations of force constants of **f** are indeterminate, since they are based on a coordinate set with redundants.¹⁹ It follows also that different **f** matrices exist which represent physically identical force fields, and consequently correspond to the same **F** matrix.

In this connection it is instructive to explain some properties of compliants and redundancy.¹ Let \mathbf{n} and \mathbf{N} denote the compliance matrices in terms of the \mathbf{r} and \mathbf{S} coordinates, respectively. Then

$$\mathbf{N} = \mathbf{F}^{-1} \quad (3)$$

but the same relation does not hold for \mathbf{n} and \mathbf{f} . It is important to notice that \mathbf{n} may be determined uniquely, in contrast to \mathbf{f} , when the force field is given, for instance in terms of \mathbf{F} . Then

$$\mathbf{n} = \mathbf{T}\mathbf{N}\mathbf{T}' = \mathbf{T}\mathbf{F}^{-1}\mathbf{T}' \quad (4)$$

The compliants possess the property of invariance.^{1,20} As a consequence the augmentation of the set of valence coordinates does not affect any of the compliants associated with the original set of valence coordinates. Another theorem from the theory of compliants states that the augmented \mathbf{n} matrix is singular; *cf.*, *e.g.*, Ref. 1. Hence this matrix is not useful in practice when an initial force field in numerical form is wanted. In particular an augmented \mathbf{n} matrix (based on a coordinate set with redundants) can never be a diagonal matrix, except in the special cases when all redundants appear explicitly as zero coordinates. Another point is worth mentioning. In the augmented \mathbf{n} matrix, in contrast to \mathbf{f} , the rows and columns corresponding to the excess coordinates can simply be erased without any physical change of the force field, which equally well is defined by the smaller compliance matrix based on the original valence coordinates without redundants. As a matter of fact the erased compliants may be determined uniquely from the remaining ones.

PRELIMINARY COMPUTATIONS FOR 1,2,5-THIADIAZOLE

Potential function The initial in-plane force field for 1,2,5-thiadiazole was constructed as an eight-constant valence force field:

$$2V = f_s(s_1^2 + s_2^2) + f_d(d_1^2 + d_2^2) + f_t t^2 + DTf_\beta(\beta_1^2 + \beta_2^2) + f_r(r_1^2 + r_2^2) + RTf_\varphi(\varphi_1^2 + \varphi_2^2) + S^2 f_\alpha \alpha^2 + DSf_\delta(\delta_1^2 + \delta_2^2) \quad (5)$$

Ref. 2 should be consulted for precise explanations of the applied notation. For the sake of convenience the in-plane valence coordinates are specified in Fig. 1. The legend of this figure includes the symmetry coordinates for the model in question, which is one of the four models treated in Ref. 2.

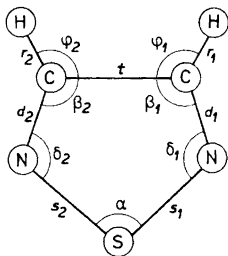


Fig. 1. The 1,2,5-thiadiazole molecule model; symmetry C_{2v} . In-plane valence coordinates are indicated. In-plane symmetry coordinates according to Ref. 2:

$$\begin{aligned} S_1(A_1) &= 2^{-\frac{1}{2}}(s_1 + s_2), & S_2(A_1) &= 2^{-\frac{1}{2}}(d_1 + d_2), \\ S_3(A_1) &= t, & S_4(A_1) &= (DT/2)^{\frac{1}{2}}(\beta_1 + \beta_2), \\ S_5(A_1) &= 2^{-\frac{1}{2}}(r_1 + r_2) \\ S_6(A_1) &= (RT/2)^{\frac{1}{2}}(\varphi_1 + \varphi_2) \\ S_1(B_2) &= 2^{-\frac{1}{2}}(s_1 - s_2), & S_2(B_2) &= 2^{-\frac{1}{2}}(d_1 - d_2) \\ S_3(B_2) &= (DT/2)^{\frac{1}{2}}(\beta_1 - \beta_2), \\ S_4(B_2) &= 2^{-\frac{1}{2}}(r_1 - r_2) \\ S_5(B_2) &= (RT/2)^{\frac{1}{2}}(\varphi_1 - \varphi_2). \end{aligned}$$

Valence force constant values. Vibrational frequencies for 1,2,5-thiadiazole were calculated from potential functions of the form (5) with tentatively chosen force constant values in a number of runs. Actually fifteen trials were made, varying one of the constants at a time. From these preliminary studies six representative sets of results are given in Table 2. Run No. 6 in this table is identical with the set of force constants used as the initial set for further refinements. The corresponding symmetry force constants are included in Table 3. The valence force constants are also found in Table 4, and Table 5 includes the corresponding calculated frequencies along with observed values.

Table 2. Valence force constants (mdyne/Å) and calculated frequencies (cm⁻¹) from preliminary calculations for 1,2,5-thiadiazole.

Run No.		1	2	3	4	5	6
	f_s	4.5	3.5	4.5	4.5	4.5	4.0
	f_d	8.0	6.0	8.0	8.0	8.0	5.8
	f_t	4.5	4.5	4.5	4.5	4.5	3.5
	f_β	1.0	1.0	1.0	1.5	1.0	1.0
	f_r	5.1	5.1	5.1	5.1	5.1	5.1
	f_φ	0.7	0.7	1.0	0.7	0.7	0.7
	f_α	1.0	1.0	1.0	1.0	1.5	1.0
	f_δ	1.0	0.5	1.0	1.0	1.0	1.0
A_1	ν_1	3065	3063	3065	3066	3066	3062
	ν_2	1661	1530	1740	1667	1688	1503
	ν_3	1260	1204	1409	1269	1274	1205
	ν_4	1138	1073	1158	1174	1159	1074
	ν_5	865	783	866	868	879	796
	ν_6	709	627	710	712	787	686
B_2	ν_1	3079	3076	3083	3089	3080	3076
	ν_2	1798	1706	1978	1854	1798	1698
	ν_3	1175	1102	1265	1241	1213	1148
	ν_4	1154	976	1159	1161	1169	1063
	ν_5	747	691	750	800	748	721

In all the tentative runs (*cf.* Table 2) f_r was kept on 5.1 mdyne/Å as a characteristic value for C—H stretching force constants,¹⁷ and $f_t = 4.5$ mdyne/Å was assumed in most of the trials. But f_t was changed to 3.5 mdyne/Å in the final run, whereby the value of ν_4 in A_1 (which also depends significantly on f_d) was improved. The lowering of f_s from 4.5 to 3.5 mdyne/Å showed mainly an influence on ν_5 in both A_1 and B_2 ; the former frequency became improved while the latter became somewhat worse when compared to the observed values (see Table 5). Changes of f_d were found to affect ν_2 and ν_3 of species A_1 , along with ν_2 , ν_3 , and ν_4 in B_2 . The change of f_β from 1.0 to 1.5 mdyne/Å gave small effect on the frequencies of A_1 , while ν_2 and ν_3 in B_2 both increased. The former became worse while the latter improved. The change of f_φ from 0.7 to 1.0 mdyne/Å affected ν_2 and ν_3 in both A_1 and B_2 , and the general

Table 3. In-plane symmetry force constants (F in mdyne/Å) and compliants (N in Å/mdyne) along with calculated frequencies (cm^{-1}) for 1,2,5-thiadiazole. The values correspond to run No. 6 of Table 2.

Species A_1		3063	1503	1205	1074	796	686
ν							
F	1	7.89					
	2	-2.06	6.89				
	3	-3.61	1.91	6.85			
	4	-5.67	3.00	5.26	10.09		
	5	0	0	0	0	5.10	
	6	0	0	0	0	0	0.70
N	1	0.218					
	2	0.012	0.168				
	3	0.034	-0.012	0.250			
	4	0.102	-0.037	-0.108	0.224		
	5	0	0	0	0	0.196	
	6	0	0	0	0	0	1.429
Species B_2		3076	1698	1148	1063	721	
ν							
F	1	4.59					
	2	0.83	6.98				
	3	0.47	0.66	1.37			
	4	0	0	0	5.10		
	5	0	0	0	0	0.70	
N	1	0.229					
	2	-0.021	0.152				
	3	-0.068	-0.066	0.783			
	4	0	0	0	0.196		
	5	0	0	0	0	1.429	

Table 4. Approximate in-plane valence force constants (mdyne/Å).

Molecule ^a	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)
f_s	4.0	5.0	3.0	4.8	6.0	4.8	6.0
f_d	5.8	5.8	5.5	5.8	5.8	3.5	3.5
f_t	3.5	3.5	3.5	4.5	4.5	3.5	3.5
f_β	1.0	1.0	1.0	1.0	1.0	1.0	1.0
f_r	5.1	5.1	5.1			5.1	5.1
f_φ	0.7	0.7	0.7			0.7	0.7
f_q				5.1	5.1	5.1	5.1
f_θ				0.7	0.7	0.7	0.7
f_α	1.0	1.5	0.5	1.5	1.8	1.5	1.8
f_δ	1.0	1.0	1.0	1.0	1.0	1.0	1.5

^a (i) 1,2,5-Thiadiazole. (ii) 1,2,5-Oxadiazole. (iii) 1,2,5-Selenadiazole. (iv) 1,3,4-Thiadiazole. (v) 1,3,4-Oxadiazole. (vi) Thiophene. (vii) Furan.

Table 5. Calculated frequencies (cm^{-1}) from approximate valence force constants (Table 4) compared to observed values.^a

Molecule	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)		
A_1 ν_1	a:	<i>3103</i>	<i>3144</i>	<i>3067</i>	<i>3036</i>	<i>3169</i>	<i>3126</i>	<i>3167</i>	
	b:	<i>3062</i>	<i>3064</i>	<i>3062</i>	<i>3071</i>	<i>3077</i>	<i>3070</i>	<i>3076</i>	
	c:	-1.3	-2.5	-0.2	1.2	-2.9	-1.8	-2.9	
	ν_2	a:	<i>1362</i>	<i>1418</i>	<i>1360</i>	<i>1393</i>	<i>1534</i>	<i>3098</i>	<i>3140</i>
		b:	<i>1503</i>	<i>1527</i>	<i>1487</i>	<i>1681</i>	<i>1698</i>	<i>3061</i>	<i>3062</i>
		c:	10	7.7	9.3	21	11	-1.2	-2.5
	ν_3	a:	<i>1249</i>	<i>1316</i>	<i>1290</i>	<i>1250</i>	<i>1495</i>	<i>1409</i>	<i>1491</i>
		b:	<i>1205</i>	<i>1275</i>	<i>1179</i>	<i>1317</i>	<i>1321</i>	<i>1610</i>	<i>1686</i>
		c:	-3.5	-3.1	-8.6	5.4	-12	14	13
	ν_4	a:	<i>1041</i>	<i>1038</i>	<i>1008</i>	<i>1231</i>	<i>1272</i>	<i>1360</i>	<i>1384</i>
		b:	<i>1074</i>	<i>1118</i>	<i>1012</i>	<i>1113</i>	<i>1040</i>	<i>1405</i>	<i>1412</i>
		c:	3.2	7.7	0.4	-9.6	-18	3.3	2.0
ν_5	a:	<i>805</i>	<i>1006</i>	<i>726</i>	<i>965</i>	<i>1092</i>	<i>1083</i>	<i>1140</i>	
	b:	<i>796</i>	<i>921</i>	<i>722</i>	<i>890</i>	<i>958</i>	<i>1160</i>	<i>1228</i>	
	c:	-1.1	-8.4	-0.6	-7.8	-12	7.1	7.7	
ν_6	a:	<i>686</i>	<i>872</i>	<i>489</i>	<i>895</i>	<i>951</i>	<i>1036</i>	<i>1066</i>	
	b:	<i>686</i>	<i>835</i>	<i>455</i>	<i>736</i>	<i>911</i>	<i>1025</i>	<i>1056</i>	
	c:	0	-4.2	-7.0	-18	-4.2	-1.1	-0.9	
ν_7	a:						<i>839</i>	<i>995</i>	
	b:						<i>837</i>	<i>891</i>	
	c:						-0.2	-10	
ν_8	a:						<i>608</i>	<i>871</i>	
	b:						<i>683</i>	<i>814</i>	
	c:						12	-6.5	
B_2 ν_1	a:	<i>3077</i>	<i>3133</i>	<i>3028</i>	<i>3075</i>	<i>3167</i>	<i>3125</i>	<i>3161</i>	
	b:	<i>3076</i>	<i>3073</i>	<i>3073</i>	<i>3066</i>	<i>3069</i>	<i>3076</i>	<i>3076</i>	
	c:	0	-1.9	1.5	-0.3	-3.1	-1.6	-2.7	
	ν_2	a:	<i>1462</i>	<i>1546</i>	<i>1385</i>	<i>1500</i>	<i>1592</i>	<i>3098</i>	<i>3129</i>
		b:	<i>1698</i>	<i>1722</i>	<i>1705</i>	<i>1623</i>	<i>1550</i>	<i>3062</i>	<i>3065</i>
		c:	16	11	23	8.2	-2.6	-1.2	-2.0
	ν_3	a:	<i>1224</i>	<i>1177</i>	<i>1234</i>	<i>1198</i>	<i>1215</i>	<i>1507</i>	<i>1556</i>
		b:	<i>1148</i>	<i>1299</i>	<i>1075</i>	<i>1308</i>	<i>1399</i>	<i>1658</i>	<i>1659</i>
		c:	-6.2	10	-13	9.2	15	10	6.6
	ν_4	a:	<i>895</i>	<i>952</i>	<i>880</i>	<i>910</i>	<i>1078</i>	<i>1256</i>	<i>1267</i>
		b:	<i>1063</i>	<i>1068</i>	<i>1026</i>	<i>1084</i>	<i>1170</i>	<i>1502</i>	<i>1462</i>
		c:	19	12	17	19	8.5	20	15
ν_5	a:	<i>779</i>	<i>889</i>	<i>589</i>	<i>741</i>	<i>925</i>	<i>1085</i>	<i>1180</i>	
	b:	<i>721</i>	<i>822</i>	<i>586</i>	<i>774</i>	<i>846</i>	<i>1204</i>	<i>1391</i>	
	c:	-7.4	-7.5	-0.5	4.5	-8.5	11	18	
ν_6	a:						<i>872</i>	<i>1040</i>	
	b:						<i>881</i>	<i>899</i>	
	c:						1.0	-14	
ν_7	a:						<i>751</i>	<i>873</i>	
	b:						<i>760</i>	<i>866</i>	
	c:						1.2	-0.8	

^a For identification of the molecules (i)-(vii), see footnote to Table 4.

a: Observed frequencies (given in italics).

b: Calculated as preliminary results from the approximate force constants.

c: Percentage deviation.

picture of calculated frequencies became somewhat worse. Also the effect of changes of f_α and f_δ from the values of 1.0 mdyne/Å used in most of the runs was studied in some details, but no general improvement was achieved; cf. runs Nos. 2 and 5 in Table 2.

Force constants and compliants. In order to illustrate some of the points from the theoretical part (see above) the final valence force field of run No. 6 in Table 2 was used to calculate the corresponding symmetry force constants and compliants. The results are shown in Table 3. Here one should notice in particular the large interaction constants associated with the ring deformation coordinates of species A_1 . Their origin is the inclusion of the extra bending coordinates in the potential energy form (5), which introduces two redundants in species A_1 and one in B_2 . By the same reason also the diagonal F constants for the ring deformations apparently have abnormally large values. This feature is most pronounced for $F_4(A_1)=10.09$ mdyne/Å, which as to the order of magnitude is ten times larger than a force constant for a bending like $S_4(A_1)$ under normal circumstances (without ring formation). But it must in the present case compensate for the extra terms in the potential energy according to eqn. (5).

It should be clear that the original valence coordinates without redundants² are mathematically sufficient to express the potential energy. But a potential function corresponding to the form (5) in terms of these coordinates must necessarily contain interaction terms, and their magnitudes can hardly be foreseen in the actual cases of practical calculations. The assumption of a valence force field in terms of the coordinates without redundants seems unrealistic. In other words an in-plane potential function as

$$2V = f_s^*(s_1^2 + s_2^2) + f_d^*(d_1^2 + d_2^2) + f_t^*t^2 \\ + DTf_\beta^*(\beta_1^2 + \beta_2^2) + f_r(r_1^2 + r_2^2) + RTf_\varphi(\varphi_1^2 + \varphi_2^2) \quad (6)$$

should not be used instead of eqn. (5). To demonstrate this point we have carried out the calculation of frequencies with the form (6) assuming $f_s^*=f_s$, $f_d^*=f_d$, etc., and using the numerical values from run No. 6 in Table 2. In this case also the symmetry \mathbf{F} matrix is diagonal, and specifically (in mdyne/Å):

$$F_1(A_1) = f_s^* + f_{ss}^* = 4.0, F_1(B_2) = f_s^* - f_{ss}^* = 4.0 \quad (7)$$

$$F_2(A_1) = f_d^* + f_{dd}^* = 5.8, F_2(B_2) = f_d^* - f_{dd}^* = 5.8 \quad (8)$$

$$F_3(A_1) = f_t^* = 3.5 \quad (9)$$

$$F_4(A_1) = f_\beta^* + f_{\beta\beta}^* = 1.0, F_3(B_2) = f_\beta^* - f_{\beta\beta}^* = 1.0 \quad (10)$$

The calculated frequencies are given in the following (in cm^{-1}). Species A_1 : 3060, 1450, 1161, 981, 783, 220. Species B_2 : 3074, 1698, 1102, 857, 710. All these values are seen to be lower than those from run 6 (see Table 2) with most significant differences for the lower frequencies. In particular the lowest (A_1) frequencies from the two sets are substantially different. The calculated lowest frequency from the potential energy form (6) is not compatible with the observed value (see Table 5), and would have been a misleading guide for the vibrational assignment.

The two forms of the potential function (5) and (6) have been discussed here in some details in order to illustrate certain properties of the compliants. The relations of the forms (7)–(10) hold unconditionally for the compliants, *i.e.* $N_1(A_1) = n_s + n_{ss}$, *etc.*, and there is no distinction between n_s and n_s^* , *etc.* This feature provides an illustration of the invariance properties of compliants mentioned in the theoretical part above. All the valence compliants n_s , n_{ss} , *etc.* may be computed from the data of Table 3. Also the elements n_α and n_δ along with the interaction terms involving α and δ coordinates may be calculated uniquely from the same data, although some relations slightly more complicated than those of eqns. (7)–(10) must be invoked.

Table 6. Observed ^a and calculated frequencies (in cm⁻¹) for in-plane species of isotopic molecules of thiophene.

		Thiophene			Thiophene-d ₄		
		Obs.	Calc.	Dev.	Obs.	Calc.	Dev.
A ₁ :	ν_1	3126	3127	0	2343	2343	0
	ν_2	3098	3104	0.2	2306	2296	-0.4
	ν_3	1409	1427	1.3	1376	1349	-2.0
	ν_4	1360	1364	0.3	1248	1259	0.9
	ν_5	1083	1072	-1.0	896	903	0.8
	ν_6	1036	1030	-0.6	785	792	0.9
	ν_7	839	844	0.6	731	736	0.7
	ν_8	608	642	5.6	585	601	2.7
B ₂ :	ν_1		3129			2335	
	ν_2	3098	3089	-0.3	2290	2297	0.3
	ν_3	1507	1532	1.7	1459	1404	-3.8
	ν_4	1256	1254	-0.2	1034	1041	0.7
	ν_5		1069		846	872	3.1
	ν_6	872	857	-1.7	752	794	5.6
	ν_7	751	754	0.4	711	650	-8.6
		Thiophene-2,5-d ₂			Thiophene-3,4-d ₂		
		Obs.	Calc.	Dev.	Obs.	Calc.	Dev.
A ₁ :	ν_1	3101	3110	0.3	3123	3120	-0.1
	ν_2	2336	2338	0.1	2314	2304	-0.4
	ν_3	1398	1403	0.4	1389	1388	0.1
	ν_4	1310	1316	0.5	1322	1306	-1.2
	ν_5	1046	1024	-2.1	1034	1061	2.6
	ν_6	884	883	-0.1	876	865	-1.3
	ν_7	754	748	-0.8	750	789	5.2
	ν_8		631		593	606	2.2
B ₂ :	ν_1	3088	3095	0.2		3124	
	ν_2		2314			2319	
	ν_3	1490	1493	0.2	1480	1468	-0.8
	ν_4	1218	1180	-3.1	1178	1160	-1.5
	ν_5	918	901	-1.9	918	988	7.6
	ν_6		807		849	838	-1.3
	ν_7		733		713	663	-7.0

^a Ref. 14.

IN-PLANE FORCE CONSTANTS

Valence force constants. It was intended to develop approximate potential functions of the form (5) for all the seven molecules of the present study. Eqn. (5) must be modified in an obvious way in order to take proper account of the various stretchings and bendings involving the H atoms in the different molecules. It was aimed at producing sets of valence force constants which should (a) be transferable between related molecules with only small changes and (b) give satisfactory agreement with the observed frequencies, in order to be useful as the initial set for further refinements. The results of these attempts are presented in Table 4. For precise definitions of the valence

Table 7. Observed ^a and calculated frequencies (in cm⁻¹) for in-plane species of isotopic molecules of furan.

		Obs.	Furan Calc.	Dev.	Obs.	Furan- <i>d</i> ₄ Calc.	Dev.
<i>A</i> ₁ :	<i>v</i> ₁	3167	3164	-0.1	2388	2382	-0.3
	<i>v</i> ₂	3140	3145	0.2	2350	2336	-0.6
	<i>v</i> ₃	1491	1492	0.1	1424	1424	0
	<i>v</i> ₄	1384	1383	-0.1	1315	1314	-0.1
	<i>v</i> ₅	1140	1121	-1.7	1054	1061	0.7
	<i>v</i> ₆	1066	1075	0.8	920	913	-0.8
	<i>v</i> ₇	995	1005	1.0	791	774	-2.1
	<i>v</i> ₈	871	886	1.7	727	727	0
<i>B</i> ₂ :	<i>v</i> ₁	3161	3162	0	2371	2371	0
	<i>v</i> ₂	3129	3127	-0.1	2327	2330	0.1
	<i>v</i> ₃	1556	1556	0	1490	1504	0.9
	<i>v</i> ₄	1267	1254	-1.0	1142	1146	0.4
	<i>v</i> ₅	1180	1199	1.6	975	939	-3.7
	<i>v</i> ₆	1040	1036	-0.4	857	840	-2.0
	<i>v</i> ₇	873	888	1.7	776	797	2.7
		Obs.	Furan-2,5- <i>d</i> ₂ Calc.	Dev.	Obs.	Furan-3,4- <i>d</i> ₂ Calc.	Dev.
<i>A</i> ₁ :	<i>v</i> ₁	3145	3157	0.4	3155	3152	-0.1
	<i>v</i> ₂	2364	2374	0.4	2361	2344	-0.7
	<i>v</i> ₃	1436	1433	-0.2	1484	1486	0.1
	<i>v</i> ₄	1357	1356	-0.1	1342	1347	0.4
	<i>v</i> ₅	1077	1091	1.3	1098	1096	-0.2
	<i>v</i> ₆	1018	1022	0.4	1053	1052	-0.1
	<i>v</i> ₇	910	887	-2.5	886	902	1.8
	<i>v</i> ₈	781	777	-0.5	732	728	-0.5
<i>B</i> ₂ :	<i>v</i> ₁	3134	3135	0	3155	3155	0
	<i>v</i> ₂		2357		2344	2344	0
	<i>v</i> ₃	1553	1547	-0.4		1514	
	<i>v</i> ₄	1212	1213	0.1	1227	1243	1.3
	<i>v</i> ₅	1060	1048	-1.1	1148	1140	-0.7
	<i>v</i> ₆	902	918	1.8	872	876	0.5
	<i>v</i> ₇	860	847	-1.5	830	814	-1.9

^a Ref. 15.

coordinates, see Ref. 2. In Table 4 the values for 1,2,5-thiadiazole are identical to those of run No. 6 in Table 2. Table 5 shows the calculated frequencies with the force constants from Table 4, and their deviations from observed values.

Table 8. Approximate out-of-plane symmetry force constants (mdyne/Å).

	1,2,5- Diazoles	1,3,4- Diazoles	Thiophene and furan
Species A_2			
F_{11}	0.42	0.42	0.42
F_{12}	-0.14	0.03	0.03
F_{13}			-0.14
F_{22}	0.22	0.22	0.22
F_{23}			0
F_{33}			0.22
Species B_1			
F_{11}	0.52	0.52	0.52
F_{12}	-0.04	0.09	0.09
F_{13}			-0.04
F_{22}	0.25	0.25	0.25
F_{23}			0
F_{33}			0.25

Table 9. Calculated frequencies (cm^{-1}) from approximate force constants (Table 8) compared to observed values.^a

Molecule		(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	
A_2	ν_1	a:	<i>881</i>	<i>824</i>	<i>868</i>	<i>880</i>	<i>941</i>	<i>898</i>	
		b:	<i>863</i>	<i>823</i>	<i>916</i>	<i>1024</i>	<i>881</i>	<i>1202</i>	<i>1106</i>
		c:	-2.0	-0.1	5.5	16	-6.4	34	
	ν_2	a:	<i>601</i>	<i>640</i>	<i>672</i>	<i>624</i>	<i>655</i>	<i>683</i>	<i>728</i>
		b:	<i>639</i>	<i>597</i>	<i>663</i>	<i>706</i>	<i>606</i>	<i>815</i>	<i>783</i>
		c:	6.3	-6.7	-1.3	13	-7.5	19	7.6
	ν_3	a:						<i>565</i>	<i>613</i>
		b:						<i>535</i>	<i>491</i>
		c:						-5.3	-20
B_1	ν_1	a:	<i>838</i>	<i>839</i>	<i>833</i>	<i>822</i>	<i>852</i>	<i>867</i>	<i>838</i>
		b:	<i>836</i>	<i>819</i>	<i>844</i>	<i>929</i>	<i>853</i>	<i>952</i>	<i>927</i>
		c:	-0.2	-2.4	1.3	13	0.1	9.8	11
	ν_2	a:	<i>520</i>	<i>631</i>	<i>438</i>	<i>485</i>	<i>625</i>	<i>712</i>	<i>745</i>
		b:	<i>523</i>	<i>565</i>	<i>522</i>	<i>519</i>	<i>481</i>	<i>793</i>	<i>787</i>
		c:	0.6	-10	19	7.0	-23	11	5.6
	ν_3	a:						<i>452</i>	<i>603</i>
		b:						<i>486</i>	<i>503</i>
		c:						7.5	-17

^a For identification of the molecules (i)–(vii), see footnote to Table 4.

a: Observed frequencies (given in italics).

b: Calculated as preliminary results from the approximate valence force constants.

c: Percentage deviation.

Final symmetry force constants. The approximate in-plane valence force fields were refined to give better agreement with the observed frequencies. For all the diazoles of the present investigation the force constants were adjusted to fit exactly the observed frequencies. For thiophene and furan, for which the frequencies for several isotopic molecules are available, an iteration procedure of least-squares fitting was employed. The final calculated frequencies for the isotopic molecules in question are shown in Tables 6 (thiophenes) and 7 (furans), including the observed frequencies and percentage deviations. The numerical values of final force constants are collected at the end of this paper.

Table 10. Observed and calculated frequencies (in cm^{-1}) for out-of-plane species of isotopic molecules of thiophene and furan.

		Thiophene			Thiophene- d_4		
		Obs.	Calc.	Dev.	Obs.	Calc.	Dev.
A_2 :	ν_1	898	893	-0.6	750	755	0.7
	ν_2	683	698	2.2	531	519	-2.3
	ν_3	565	565	0		497	
B_1 :	ν_1	867	865	-0.2	684	687	0.4
	ν_2	712	712	0	531	531	0
	ν_3	452	450	-0.4	414	409	-1.2
		Thiophene-2,5- d_2			Thiophene-3,4- d_2		
		Obs.	Calc.	Dev.	Obs.	Calc.	Dev.
A_2 :	ν_1		892			769	
	ν_2		583			669	
	ν_3		516			497	
B_1 :	ν_1	819	820	0.1	811	811	0
	ν_2	584	585	0.2	587	587	0
	ν_3	419	413	-1.4	442	438	-0.9
		Furan			Furan- d_4		
		Obs.	Calc.	Dev.	Obs.	Calc.	Dev.
A_2 :	ν_1		865			725	
	ν_2	728	726	-0.3	572	574	0.3
	ν_3	613	611	-0.3		511	
B_1 :	ν_1	838	835	-0.4	700	704	0.6
	ν_2	745	752	0.9	597	586	-1.8
	ν_3	603	588	-2.5	500	494	-1.2
		Furan-2,5- d_2			Furan-3,4- d_2		
		Obs.	Calc.	Dev.	Obs.	Calc.	Dev.
A_2 :	ν_1		848		780	780	0
	ν_2	644	645	0.2		667	
	ν_3	524	534	1.9	527	540	2.5
B_1 :	ν_1	799	803	0.5	806	806	0
	ν_2	679	674	-0.7	605	600	-0.8
	ν_3	506	495	-2.2	587	581	-1.0

Table 11. Final symmetry force constants (mdyne/Å) for diazoles.^a

		1,2,5- Thia- diazole	1,2,5- Oxa- diazole	1,2,5- Sena- diazole	1,3,4- Thia- diazole	1,3,4- Oxa- diazole
In-plane						
A_1 :	F_{11}	7.851	14.051	5.465	10.638	20.617
	F_{12}	-1.913	-2.458	-1.243	-0.986	-5.495
	F_{13}	-3.609	-7.471	-2.142	-4.940	-11.375
	F_{14}	-5.631	-11.280	-3.386	-7.199	-15.505
	F_{15}	0.002	0.064	0.014	0.048	0.188
	F_{16}	0.105	0.164	0.053	0.408	0.817
	F_{22}	6.501	6.871	6.321	6.577	9.124
	F_{23}	2.058	2.720	1.253	2.028	5.308
	F_{24}	2.824	3.370	1.918	1.875	6.936
	F_{25}	-0.002	0.032	0.004	-0.077	-0.028
	F_{26}	-0.234	-0.176	-0.316	-0.357	-0.619
	F_{33}	6.895	10.293	5.402	9.922	15.474
	F_{34}	5.424	9.800	3.111	7.514	13.404
	F_{35}	-0.006	-0.022	-0.013	0.080	-0.021
	F_{36}	-0.003	-0.062	0.082	-0.208	-0.396
	F_{44}	9.859	15.553	6.495	12.755	21.091
	F_{45}	0.026	0.003	-0.007	0.029	-0.039
	F_{46}	-0.118	-0.045	-0.120	-0.172	-0.506
	F_{55}	5.234	5.370	5.117	4.981	5.409
	F_{56}	-0.003	-0.009	0.005	-0.021	-0.040
F_{66}	0.691	0.693	0.731	0.602	0.840	
B_2 :	F_{11}	5.193	4.802	3.515	4.654	5.737
	F_{12}	0.604	0.386	0.057	0.432	-0.353
	F_{13}	0.426	0.020	0.373	0.330	0.104
	F_{14}	0.013	0.067	-0.004	-0.100	-0.149
	F_{15}	0.115	-0.049	0.171	0.053	-0.172
	F_{22}	5.083	5.788	4.849	5.425	6.499
	F_{23}	0.656	0.779	0.066	0.523	0.796
	F_{24}	-0.100	-0.092	-0.016	-0.134	-0.105
	F_{25}	0.092	0.052	-0.262	0.080	-0.011
	F_{33}	1.483	1.448	1.274	1.206	1.490
	F_{34}	0.001	0.014	0.011	-0.043	-0.006
	F_{35}	0.147	0.057	0.222	0.008	-0.096
	F_{44}	5.086	5.286	4.933	5.114	5.414
	F_{45}	-0.056	-0.036	-0.078	-0.002	-0.024
	F_{55}	0.563	0.573	0.615	0.587	0.619
	Out-of-plane					
A_2 :	F_{11}	0.382	0.481	0.416	0.319	0.487
	F_{12}	-0.112	-0.167	-0.155	0.029	0.038
B_1 :	F_{22}	0.209	0.233	0.219	0.168	0.253
	F_{11}	0.515	0.646	0.374	0.487	0.872
	F_{12}	-0.039	-0.059	-0.008	0.038	0.183
	F_{22}	0.251	0.265	0.236	0.253	0.274

^a Fit exactly to the observed frequencies.

Table 12. Final symmetry force constants (mdyne/Å) for thiophene and furan.

In-plane Species:	Thiophene		Furan	
	A_1	B_2	A_1	B_2
F_{11}	8.088	4.804	14.716	6.542
F_{12}	-2.224	-0.588	-1.883	0.318
F_{13}	-3.306	-0.126	-7.837	0.317
F_{14}	-4.737	-0.119	-11.829	-0.168
F_{15}	0	0.060	0.158	0.353
F_{16}	-0.038	-0.016	0	-0.033
F_{17}	0.199	0.080	0.311	-0.216
F_{18}	0.390		0	
F_{22}	5.664	4.257	4.658	6.532
F_{23}	2.021	0.440	2.632	0.829
F_{24}	3.066	-0.083	3.523	-0.277
F_{25}	-0.520	0.025	-0.058	0.056
F_{26}	-0.030	-0.142	0.044	-0.373
F_{27}	-0.117	-0.094	-0.125	-0.245
F_{28}	0.058		0.052	
F_{33}	7.263	1.310	12.981	1.459
F_{34}	5.567	-0.070	12.327	-0.051
F_{35}	-0.053	0.033	0	0.013
F_{36}	-0.025	-0.112	0.075	-0.068
F_{37}	0.036	0.042	-0.166	0.148
F_{38}	-0.013		0.136	
F_{44}	9.761	5.288	19.667	5.345
F_{45}	0.399	-0.017	-0.273	-0.026
F_{46}	0.008	-0.038	0.082	-0.044
F_{47}	-0.068	-0.004	-0.241	-0.021
F_{48}	0.044		0.204	
F_{55}	5.246	5.161	5.320	5.310
F_{56}	-0.021	0.027	0	0.007
F_{57}	-0.016	-0.020	-0.024	-0.022
F_{58}	-0.117		0.017	
F_{66}	5.260	0.526]	5.418	0.632
F_{67}	0.004	0.044	0	0.059
F_{68}	0		0	
F_{77}	0.453	0.546	0.608	0.524
F_{78}	-0.020		0.025	
F_{88}	0.614		0.524	

Out- of-plane Species:	Thiophene		Furan	
	A_2	B_1	A_2	B_1
F_{11}	0.383	0.492	0.530	0.709
F_{12}	0.128	0.185	0.142	0.203
F_{13}	-0.184	-0.104	-0.232	-0.097
F_{22}	0.168	0.227	0.214	0.248
F_{23}	-0.019	-0.034	-0.048	-0.013
F_{33}	0.292	0.243	0.278	0.241

OUT-OF-PLANE FORCE CONSTANTS

The F matrix blocks of the out-of-plane species of the considered molecules are relatively small, and it was assumed that the analysis could be performed in terms of the symmetry coordinates throughout.

Preliminary calculations showed a satisfactory fit to observed frequencies for all the 1,2,5-thiadiazoles when using the same set of harmonic force constants for the three molecules in question. The diagonal terms of this force field were also successfully transferred to the two 1,3,4-diazoles, but the interaction F'_{12} force constant in both species was changed. These preliminary force fields are found in Table 8, and the corresponding calculated frequencies are included in Table 9, along with the observed frequencies and percentage deviations. The values of force constants from the approximate force fields of diazoles were also tentatively transferred to thiophene and furan; see Table 8. The resulting calculated frequencies gave a rather poor fit to the observed values; see Table 9. Nevertheless the force field was adopted as the initial set, as it was assumed to be sufficiently accurate as a starting point in the least-squares procedure of fitting to all the available frequencies for isotopic thiophene and furan molecules.

The final sets of force constants were obtained by the same procedures as used in the case of the in-plane force fields (*cf.* preceding section). For the final calculated frequencies for isotopic thiophene and furan molecules, including observed frequencies and percentage deviations, see Table 10.

NUMERICAL FINAL FORCE CONSTANTS

The numerical values of final force constants of the present investigation are collected in Table 11 (diazoles) and 12 (thiophene and furan), including both the in-plane and out-of-plane constants. They are the symmetry force constants consistent with the symmetry coordinates specified in Ref. 2.

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