Transferability and Physicochemical Interpretation of Canonical Force Fields in Redundant Internal Coordinates: Pyridazine and 3,6-Dichloropyridazine

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The behavior of various force fields for pyridazine and 3,6-dichloropyridazine coming from different origins (i.e., HF/6-31G*, MP2/6-311G**, BLYP/6-31G*, B3LYP/6-31G* previously scaled) and empirical force fields transferred from the benzene molecule is investigated. These potentials are subjected to a linear least-squares refinement with the available experimental information considered as observed data. Moreover, the transferability properties of the force fields for these related molecules are analyzed. From the refined force fields which gave the most satisfactory results in the fitting procedure, the physicochemical meaning of the force constants in terms of redundant simple internal coordinates in the unambiguous *canonical* form is studied. Although the results are not completely decisive for the pyridazine series, significant conclusions are drawn pertaining to their force fields, some of which are calculated for the first time. First, the utility of canonical force fields is shown through the force fields tranferred from benzene, which produce results for some symmetry blocks that are comparable to those obtained from quantum mechanical force fields. Second, we report the refined force fields in simple valence internal coordinates and observe that they give values for the ring-stretching force constants that agree with the electronic structure of this molecule, for which the aromatic character is shifted toward one of the Kekulé structures that has double bonds between the C and N atoms and in the CC meta bond. All of this is in accordance with the low aromatic character of the pyridazine ring, especially as compared with the other azines. In addition, the calculated values for the torsion and CH and CCl bending force constants also are explained in the electronic structure of these systems.

I. Introduction

Since the 1950s when the first reference books on molecular vibrations were published,[1] the understanding of vibrational analysis has continued in permanent and deep evolution. Even the most elementary approach in the field (i.e., the harmonic or quadratic description of the molecular potential) has had new and significant contributions in very recent years. Specifically, one of the most controversial topics in the field has been the selection of an appropriate coordinate set to describe molecular vibrations and harmonic force constants. For a long time, force fields in terms of redundant simple valence internal coordinates (VICs) were rejected because of a number of disadvantages[2] including, in the harmonic approximation, the *indeterminacy* of the kinetic (**G**) and potential (**F**) molecular energy matrices.[1−3] This limitation led to the selection of independent (symmetry, pseudosymmetry, or internal) coordinate sets for the molecular potential, although this choice lost part of the physicochemical meaning and the transferability of the force constants.

At the same time, other groups have supported a uniquely defined set of force constants referred to as redundant coordinates,[3,4] and in recent years, the number of researchers using this kind of coordinate basis in their studies has increased. For example, Pulay and Fogarasi[5] developed a gradient geometry optimization procedure in terms of redundant VICs. Baker et al.[6,7] are working on the derivation of scaled quantum mechanical force fields (SQM) involving the direct scaling of individual primitive valence force constants from a full set of redundant VICs. Also, algorithms using redundant curvilinear coordinates to calculate frequencies along a reaction path have been presented,[8] and new methods to resolve the inverse problem of vibrational spectroscopy on the basis of Tikhonov's method of regularization and use of redundant systems of VICs have been described.[9] Very recently, Martínez Torres et al.[10] have succeeded in the development of an unambiguous formalism for molecular vibrations in terms of redundant VICs by using canonical matrices in defining canonical force fields, which provide a more coherent and generalized treatment than those found in the previous literature.[4b,h] Their definitions were extended to other matrices, which are also affected by the problem of indeterminacy when redundant coordinates are used

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Canonical Force Fields

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(i.e., the kinetic energy matrices and those matrices involved in transforming different sets of vibrational coordinates). Their results proved the mathematical unambiguity of the canonical force field in terms of redundant VICs.[10] Thus, they have offered a powerful tool to test the physicochemical meaning of the force constants in this coordinate set as well as the transference and interpolation possibilities of the force fields between related molecular systems.

There are two possible methods to calculate molecular harmonic force fields: quantum chemical determinations and empirical force fields. Quantum mechanical force fields are mainly represented by two approaches: ab initio and density functional theory (DFT) methods. One of the most accurate approaches in ab initio methods is coupled cluster theory with single and double excitation plus quasiperturbative triple excitation, CCSD(T),[11] together with the use of correlation consistent basis sets with high angular momentum functions[12] with which it is possible to obtain a high level of accuracy in the prediction of molecular harmonic wavenumbers and force fields.[13] However, this kind of calculation imposes a high computational cost, which can presently be undertaken only for quite small molecules. Thus, Hartree−Fock methods and modest electron correlation treatments, for instance, second-order Møller−Plesset perturbation theory together with standard double and triple split valence basis sets,[14] have become a routine way to calculate molecular properties, although their results do not reproduce the experimental evidence with high accuracy. DFT methods[15] constitute a computationally cheaper option, the results of which reach a notable accuracy for many molecular properties.[16] However, the definition of DFT functionals is somewhat arbitrary, and the improvement of these functionals requires the inclusion of empirical parameters whose values must be refined using, as a reference, a more or less extensive series of molecular properties.[17]

Empirical force fields provide a solution to the vibrational problem where it is usual to find fewer observed data than parameters (force constants) which have to be determined. In such a case, it is possible to resort to a simplex method,[18] a traditional linear[19] or nonlinear[20] least-squares method, or a regularization treatment[9] such as iterative techniques to give one of the possible solutions of the secular equation. In any case, it is necessary to choose an a priori matrix of force constants as an initial approximation which could come, in principle, from three different sources: empirical force fields transferred from related molecules, quantum mechanical force fields from a particular level of theory, and theoretical and semiempirical force fields previously scaled by using a typical scaling technique.[6,7,21]

In this paper, our first aim is to investigate the behavior of various force fields from different origins when they are subjected to a linear least-squares refinement, considering as observed data the available experimental information of the studied molecules. First, we also want to test the transferability properties of the force fields belonging to related molecules. Second, from those force fields which give the most satisfactory results in the refinement procedure, we will analyze the physicochemical meaning of the force constants when these harmonic potentials are expressed as canonical force fields[10] in terms of redundant VICs. To understand the nature of a canonical force field in a molecule with n vibrational degrees of freedom, n internal coordinates are necessary and sufficient to determine the displacements of the nuclei from their equilibrium positions, and the definition of any force field in the harmonic approach needs $n(n + 1)/2$ independent param-

eters. If for some reason (e.g., molecular symmetry) a number of m internal coordinates are considered, where $m > n$, they must satisfy $m - n$ constraint conditions (redundancy relationships) which rise from the molecular geometry. In such a case, the force field would be a function of $m(m + 1)/2$ parameters. Because there are more parameters than those needed to define the force field, it is said that the force field in redundant coordinates is undetermined (i.e., there are infinite sets of values of such force constants that give a correct harmonic potential energy surface). However, the indeterminacy of the force field can be avoided if *all* of the m internal coordinates are considered as independent variables. The latter can be done by transferring molecular geometry constraints (previously imposed on the internal coordinates, which are now considered independent) to the force constants; then, $[m(m + 1) - n(n + 1)]/2$ additional relations between the force constants (sum rule relationships) can be obtained, which make a uniquely determined force field[4b,10] possible. These sum rule relationships are represented by algebraic combinations of force contants, which contribute with a value of zero to the potential energy and imply no molecular deformation. A force field so defined is the canonical force field. Thus, the treatment reduces a problem with redundant coordinates and undetermined force constants to a problem with independent coordinates and determined force constants.

The pyridazine (1,2-diazine) and 3,6-dichloropyridazine molecules were selected for this study. Although there is not extensive experimental vibrational information on these compounds, they constitute attractive molecules from the point of view that they represent a typical example of systems with cyclic redundant relationships, besides being a good series to check the transference of the force fields between related molecules. In particular, for each molecule, three types of initial force fields were tested in the empirical least-squares procedure: first, a group of three quantum mechanical force fields at the Hartree−Fock level (HF/6-31G*), with a partial electron correlation treatment through second-order Møller−Plesset perturbation theory (MP2/6-311G**) and under the density functional approximation (BLYP/6-31G*); second, a scaled B3LYP/6-31G* quantum mechanical force field; third, empirical force fields transferred from the benzene molecule. The transference possibilities between related molecules of the various force fields are checked and analyzed, specifically, the force field transferability from benzene to the two pyridazines and from pyridazine to its chlorinated derivative. Moreover, we emphasize that the description of the molecular vibrational force fields in terms of VICs in canonical form is decisive for the transference procedures to the extent of making the physicochemical interpretation of the force constants possible.

II. Method

Although pyridazine and 3,6-dichloropyridazine have not been as widely studied as pyrimidine and pyrazine and their chlorinated derivatives, they have recently aroused interest in several research groups. (See refs 22 and 23 and references therein to find a broad survey of the vibrational background of these systems.)

II.1. Definition of Coordinates. Pyridazine and 3,6-dichloropyridazine[23−31] belong to the structural C_{2v} symmetry point group.[32] The experimental structures selected in the present study are taken from refs 27 and 28 for pyridazine and 3,6-dichloropyridazine, respectively. The definitions of internal coordinate [i.e., bond stretching, angle bending,[2a] and out-of-plane (molecular plane) displacements of the H atoms (wagging)][2a] and torsion[33] and axis orientation are shown in
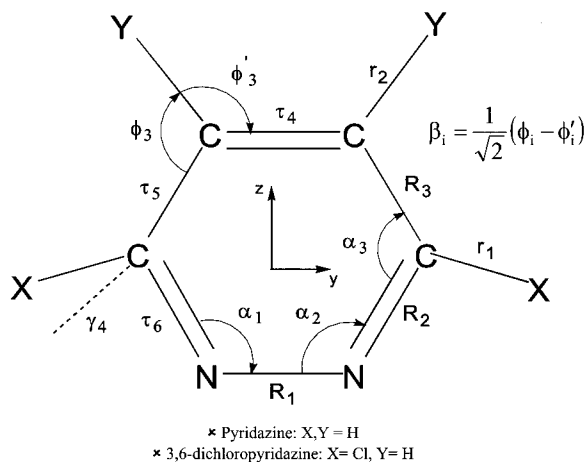
$$\beta_i = \frac{1}{\sqrt{2}}(\phi_i - \phi_i')$$

Figure 1. Valence internal coordinates (VIC) in the pyridazine series: γ is the out-of-plane displacement of H atoms (wagging coordinate) and τ is ring torsion[33] around the bond indicated. In the wagging coordinates, the H atoms move in the positive X direction. The torsions consider not only the ring contribution but also the contributions of the CH bond to the torsional displacement.

Figure 1. As usual,[1] the CH-bending internal coordinates are defined as the normalized difference between Φ_i and Φ_i'. In this way, 30 VICs are defined for each molecule and, because there are only 24 vibrational degrees of freedom ($3N - 6$), six redundancy relationships appear which are distributed in symmetry species as $2A_1 + 2A_2 + B_1 + B_2$. Because, in principle, there are a larger number of parameters (force constants) to be refined when the force field is expressed in dependent instead of independent coordinates, we proceeded to eliminate the redundancies. Thus, a new set of independent symmetry coordinates (ISCs) to express the force fields and carry out the refinement is defined.

The redundancy relationships are derived through the $\mathbf{BB}^T$ diagonalization,[34] where $\mathbf{B} = \mathbf{Ub}$, $\mathbf{U}$ is the matrix of ($M \times M$) [(30×30)] order which expresses the dependent symmetry coordinates[2a] as functions of the VICs, $\mathbf{b}$ is the matrix of ($M \times 3N$) [(30×30)] order which defines the internal coordinates R_i ($i = 1-M$, M is the number of internal coordinates), and the superindex T denotes the transpose. Those eigenvectors with null eigenvalues represent the redundancy relationships and are available as Supporting Information: Tables IS and IIS for pyridazine and 3,6-dichloropyridazine, respectively. (Tables denoted by "S" present additional information deposited as Supporting Information.) The independent symmetry coordinates were obtained by orthonormalization with respect to the redundancy relationships using the Gram−Schmidt[35] procedure, and their algebraic forms and the values of their coefficients are shown in Tables 1 and 2, respectively. These forms guarantee[10] all of the necessary conditions to transform the force fields from ISCs to VICs in canonical form.

The $\mathbf{b}$ matrices were calculated from the selected experimental structure mentioned above for each molecule. This calculation, those concerning $\mathbf{Ub}$ and $\mathbf{BB}^T$ products, and the diagonalization procedure were carried out with the VIBRA program.[36] The MATHEMATICA program[37] was used to apply the Gram−Schmidt procedure.

II.2. Selected Experimental Data. The observed data to be fitted in the least-squares refinement are the experimental anharmonic vibrational wavenumbers of pyridazine-h_4[22,23] and 3,6-dichlropyridazine[23] (ν_i; Table 3) and the wavenumbers (ν_i) of the two deuterated species pyridazine-$3,6$-d_2 and pyridazine-d_4 whose experimental data are selected from ref 38. However, on the basis of our previous experience with SQM force fields

TABLE 1: Independent Symmetry Coordinates of Pyridazine and 3,6-Dichloropyridazine[a]

A₁ Symmetry

$S_1 = a(r_1 + r_4)$
$S_2 = a(r_2 + r_3)$
$S_3 = b(R_2 + R_6) + c(R_3 + R_5) - dR_1 + eR_4 - f(\alpha_1 + \alpha_2) - g(\alpha_3 + \alpha_6) + \boldsymbol{h}(\alpha_4 + \alpha_5)$
$S_4 = \boldsymbol{i}(R_3 + R_5) + jR_1 - kR_4 + l(\alpha_1 + \alpha_2) + \boldsymbol{m}(\alpha_3 + \alpha_6) - \boldsymbol{n}(\alpha_4 + \alpha_5)$
$S_5 = \boldsymbol{o}R_1 + \boldsymbol{p}R_4 - q(\alpha_1 + \alpha_2) - \boldsymbol{r}(\alpha_3 + \alpha_6) + s(\alpha_4 - \alpha_5)$
$S_6 = tR_4 + u(\alpha_1 + \alpha_2) + \mathbf{v}(\alpha_3 + \alpha_6) - \boldsymbol{w}(\alpha_4 + \alpha_5)$
$S_7 = x(\alpha_1 + \alpha_2) - \boldsymbol{y}(\alpha_3 + \alpha_6) + \mathbf{z}(\alpha_4 + \alpha_5)$
$S_8 = \boldsymbol{a}(\beta_1 - \beta_4)$
$S_9 = \boldsymbol{a}(\beta_2 - \beta_3)$

A₂ Symmetry

$S_{10} = a'(\gamma_1 - \gamma_4) - b'(\gamma_2 - \gamma_3) - c'\tau_1 + d'\tau_4 - e'(\tau_2 + \tau_6) + f'(\tau_3 + \tau_5)$
$S_{11} = g'(\gamma_2 - \gamma_3) - h'\tau_1 + i'\tau_4 - j'(\tau_2 + \tau_6) + k'(\tau_3 + \tau_5)$
$S_{12} = l'\tau_1 + m'\tau_4 - n'(\tau_2 + \tau_6) - o'(\tau_3 + \tau_5)$
$S_{13} = p'\tau_4 + q'(\tau_2 + \tau_6) - r'(\tau_3 + \tau_5)$

B₁ Symmetry

$S_{14} = s'(\gamma_1 + \gamma_4) + t'(\gamma_2 + \gamma_3) + u'(\tau_2 - \tau_6) + \mathbf{v}'(\tau_3 - \tau_5)$
$S_{15} = w'(\gamma_2 + \gamma_3) - \boldsymbol{x}'(\tau_2 - \tau_6) - \boldsymbol{y}'(\tau_3 - \tau_5)$
$S_{16} = z'(\tau_2 - \tau_6) - a''(\tau_3 - \tau_5)$

B₂ Symmetry

$S_{17} = a(r_1 - r_4)$
$S_{18} = a(r_2 - r_3)$
$S_{19} = b''(R_2 - R_6) - c''(R_3 - R_5) + d''(\alpha_1 - \alpha_2) - e''(\alpha_3 - \alpha_6) - f''(\alpha_4 - \alpha_5)$
$S_{20} = g''(R_3 - R_5) + h''(\alpha_1 - \alpha_2) - \boldsymbol{i}''(\alpha_3 - \alpha_6) - \boldsymbol{j}''(\alpha_4 - \alpha_5)$
$S_{21} = k''(\alpha_1 - \alpha_2) + \boldsymbol{l}''(\alpha_3 - \alpha_6) + \boldsymbol{m}''(\alpha_4 - \alpha_5)$
$S_{22} = n''(\alpha_3 - \alpha_6) - \boldsymbol{o}''(\alpha_4 - \alpha_5)$
$S_{23} = a(\beta_1 + \beta_4)$
$S_{24} = a(\beta_2 + \beta_3)$

[a] Numerical values of the symmetry coordinate coefficients are reported in Table 2 for pyridazine and 3,6-dichloropyridazine.

on these isotopes, in some cases, the fundamentals are assigned to bands different from those proposed initially by Stidham and Tucci.[38] The final assignment used in this work is presented in Table 3 for pyridazine-$3,6$-d_2 and -d_4. Only the fundamentals with the lowest experimental uncertainties are considered in the refinement. The refinement was carried out using the fundamental frequencies of all of the species as data rather than frequencies for the normal species and isotopic shift for deuterated derivatives.

II.3. Initial Force Fields To Be Refined. Force fields of three different types are used as starting points in the refinement procedure (i.e., unscaled and scaled quantum mechanical force fields and empirical force fields transferred from related molecules). A flow diagram is displayed in Figure 2 where all of the force fields tested for each molecule as well as the various transfers of the potentials carried out between molecules can be seen.

The GAUSSIAN92[39] and GAUSSIAN94[40] packages were used to calculate the fully optimized geometries, harmonic vibrational wavenumbers, and quantum mechanical force fields of pyridazine and 3,6-dichloropyridazine. The structures corresponding to the minimum of energy with respect to the displacements of the nuclear coordinates were obtained by the simultaneous relaxation of all of the geometric parameters. The harmonic vibrational wavenumbers and force constants of the two molecules were calculated from analytical second derivatives of the potential energies (see Figure 2 for details of the different levels of calculations used). The quantum mechanical force fields in Cartesian coordinates were transformed to ISCs (Table 1) by using the VIBRA program[36] in accordance with the relation presented in ref 10.

SQM force fields obtained for these two molecules from ref 23 were also used as an initial starting point in the refinement

TABLE 2: Numerical Values of the Coefficients of the Independent Symmetry Coordinates (ISC) of Pyridazine and 3,6-Dicloropyridazine[a]

	pyridazine	3,6-dichloropyridazine		pyridazine	3,6-dichloropyridazine		pyridazine	3,6-dichloropyridazine
a	0.707 107	0.707 007	a′	0.649 655	0.650 980	a″	0.494 092	0.495 845
b	0.687 319	0.688 029	b′	0.074 151	0.073 083	b″	0.640 614	0.638 931
c	0.036 972	0.036 439	c′	0.215 203	0.216 816	c″	0.143 212	0.145 973
d	0.081 826	0.080 817	d′	0.232 493	0.228 233	d″	0.107 316	0.109 530
e	0.081 828	0.080 817	e′	0.101 408	0.100 447	e″	0.212 686	0.213 964
f	0.097 662	0.096 061	f′	0.109 469	0.106 037	f″	0.111 137	0.112 614
g	0.002 267	0.001 413	g′	0.681 680	0.681 851	g″	0.620 939	0.619 598
h	0.099 929	0.097 606	h′	0.145 959	0.148 040	h″	0.138 100	0.140 598
i	0.689 369	0.689 245	y′	0.166 009	0.164 535	i″	0.273 695	0.274 653
j	0.079 524	0.080 256	j′	0.066 770	0.066 451	j″	0.143 017	0.144 557
k	0.079 526	0.080 256	k′	0.080 137	0.078 555	k″	0.645 499	0.644 102
l	0.094 916	0.095 503	l′	0.699 958	0.694 197	l″	0.255 846	0.258 197
m	0.002 204	0.001 512	m′	0.246 033	0.251 640	m″	0.133 689	0.135 895
n	0.097 119	0.096 834	n′	0.473 933	0.476 679	n″	0.327 478	0.329 336
o	0.933 993	0.933 215	o′	0.012 280	0.012 710	o″	0.626 704	0.625 731
p	0.136 681	0.138 357	p′	0.639 629	0.637 420			
q	0.163 130	0.164 564	q′	0.179 321	0.181 880			
r	0.003 787	0.002 524	r′	0.513 109	0.513 584			
s	0.155 918	0.167 019	s′	0.706 768	0.706 941			
t	0.923 935	0.922 903	t′	0.008 403	0.005 892			
u	0.189 043	0.192 474	u′	0.014 119	0.009 935			
v	0.004 389	0.285 774	v′	0.014 455	0.010 100			
w	0.193 431	0.193 926	w′	0.652 904	0.652 895			
x	0.298 554	0.295 195	x′	0.189 716	0.190 405			
y	0.577 236	0.577 301	y′	0.194 227	0.193 582			
z	0.278 682	0.282 110	z′	0.505 839	0.504 121			

[a] See Table 1 for a description of the symmetry coordinates.

TABLE 3: Fundamental Wavenumbers (ν_i, cm^{-1}) of Pyridazine, Two of Its Deuterated Species, and 3,6-Dichloropyridazine[a]

	pyridazine[b]		pyridazine-d_4[c]			pyridazine-3,6-d_2[c]			3,6-dichloropy[c]	
	ν_i	Δ	ref 38, ν_i	this work, ν_i	Δ	ref 38, ν_i	this work, ν_i	Δ	ν_i	Δ
				A$_1$ Symmetry						
ν_1	3086	7.8	2303	2303	2.5	3053	3070[d]	3.8	3091[e]	0.1
ν_2	3071	1.1	2277	2277	3.5	2293	2293	1.8	1556	1.1
ν_3	1570	0.0	1549	1549	5.9	1556	1556	6.7	1299	0.8
ν_4	1444	2.9	1272	1319[d]	2.4	1392	1352[d]		1168	4.5
ν_5	1160	0.8	1203	1125[d]			1114	1145[d]	1147	3.1
ν_6	1119	0.7	951	951	0.3		1044[d]		1045	8.6
ν_7	1061	0.1	896	833	0.4	958	958	2.8	780	1.8
ν_8	968	2.9	833	805[d]		856	856	11.2	343	1.0
ν_9	665	5.7	608	638[d]	7.1	626	661[d]	4.8	232	0.1
				A$_2$ Symmetry						
ν_{10}	1025[f]		766	849[d]		840	937[d]	7.3	983	
ν_{11}	945	7.1	727	766	1.6	806	806	0.2	741	
ν_{12}	754	0.8	686	686	17.2	730	730	14.0	407	
ν_{13}	367	3.2	351	351		383	383		298	
				B$_1$ Symmetry						
ν_{14}	987	9.6	710	796[d]		755	888[d]		836	
ν_{15}	745	0.9	563	563	3.1	665	665	8.9	507	
ν_{16}	376	3.7	326	326	1.8	332	332	1.8	114/156[g]	
				B$_2$ Symmetry						
ν_{17}	3079	11.9	2303	2282[d]	0.9	3065	3057[d]	2.4	3074[e]	0.0
ν_{18}	3057	0.3	2259	2259	3.2	2286	2286	8.5	1528	2.3
ν_{19}	1563	1.7	1528	1528	3.5	1543	1543	0.6	1387	1.1
ν_{20}	1413	1.8	1318	1272[d]	6.6	1423	1392[d]	4.4	1129	12.6
ν_{21}	1281	8.1	1038	1018[d]		1178	1082[d]		1019	8.1
ν_{22}	1049	4.4	973	973	7.6	1019	1019	5.9	628	1.1
ν_{23}	1027[f]	0.3	853			888	910[d]		555	3.9
ν_{24}	622	4.1	639	608[d]	1.1	661	626[d]	5.4	372	0.9

[a] Δ represents differences between the observed wavenumbers included in the refinement and their calculated values using the MP2/6-31G** force field ($\Delta = |\nu_{obs} - \nu_{cal}|$). For out-of-plane vibrations of 3,6-dichloropyridazine, the vibrational secular equation was directly solved. [b] Experimental wavenumbers were selected from the gas-phase spectra; when they were not available, data from liquid and solid phases were used.[22] [c] Wavenumbers selected from the IR spectra; when these data were not available, the information from Raman spectra was used.[23,38] [d] Different assignment from that proposed by Stidham and Tucci.[38] [e] Unperturbed wavenumbers calculated considering the Fermi resonance.[23] [f] Both fundamentals show close wavenumbers; see the discussion in ref 22. [g] Two possible bands to assign to this fundamental.

procedure. In particular, the SQM force fields denoted as set BI for pyridazine and set BII for 3,6-dichloropyridazine in ref 23 were selected. Those SQM potentials were obtained accord-

ing to Pulay's method[41] (i.e., scale factors associated with each diagonal force constant were refined by least-squares fitting to every kind of vibrational datum, fundamental frequencies in the
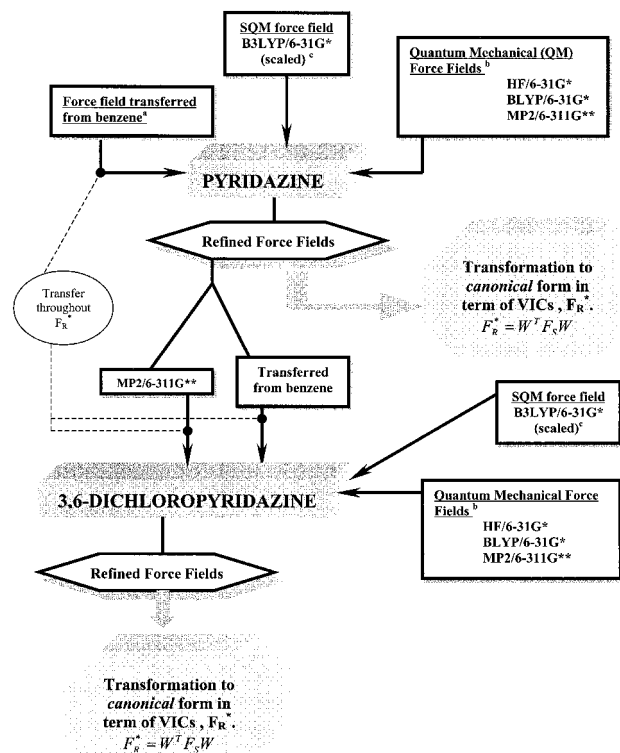
Figure 2. Flow diagram of the various force fields tested for pyridazine and 3,6-dichloropyridazine, as well as the transfers of the harmonic potentials done between different molecules. (Footnotes: (a) Reference 43. (b) Conventional ab initio methods at the Hartree−Fock[60] level and Møller−Plesset perturbation theory[61] of the second order as well as density funcitonal theory methods in the Kohn−Sham formulation[62] with different exchange-correlation functionals[63,64] were used. With each method, a series of standard split valence basis sets was used.[65−67] (c) Scaled force field from ref 23.)

present case, that stemmed from the force field). Set BI included six scaled factors for pyridazine, and set BII included nine scaled factors for 3,6-dichloropyridazine. These scaled force fields in terms of the independent internal coordinates of Pulay et al.[42] ($\mathbf{U}_1$) were expressed in terms of the ISCs sets defined in this work ($\mathbf{W}_2$; Table 1) by using eq 1 where the $\mathbf{U}$ matrix has been

$$F_{S_2} = \mathbf{W}_2\mathbf{U}_1{}^T F_{S_1} \mathbf{U}_1 \mathbf{W}_2{}^T \qquad (1)$$

defined as orthogonal.

Finally, with respect to those empirical force fields transferred from related molecules, the different cases tested are outlined in Figure 2. In particular, the complete empirical harmonic force field of benzene proposed by Goodman et al.[43] was selected to be transferred to pyridazine. Two refined force fields of pyridazine were transferred to 3,6-dichloropyridazine: the force field initially transferred from benzene and the refined MP2/6-311G** force field. Both potentials were selected because they gave the most favorable results and they represented, among the force fields tested, an example of empirical and theoretical force fields, respectively. The transfers were carried out in the following two steps:

(1) The force fields of the *reference molecule* must be expressed in terms of independent symmetry coordinates and then be transformed to the simple valence internal ones in canonical form. This procedure involves defining the $\mathbf{W}$ transformation matrix ($3N − 6$, M) between redundant VICs and ISCs,[3,4b,10] which should be orthogonal to the redundancy relationships. Then, $\mathbf{W}$ is used to transform the force constants

expressed in ISCs[3,4b,10] (F_S) to force constants in VICs ($F_R{}^*$) using the expression

$$F_R{}^* = \mathbf{W}^T F_S \mathbf{W} \qquad (2)$$

$F_R{}^*$ is the canonical vibrational force field. In the present work, we used the MATHEMATICA program[37] to carry out the above transformation.

For benzene, it should be noted that the $\mathbf{W}$ matrix is constructed starting from the symmetry coordinates defined by Duinker and Mills[44] (series 2, $\mathbf{W}_2$) for the in-plane vibrations and from a new symmetry coordinate set defined in the present work for the out-of-plane movements. The new set was obtained using the experimental geometry from ref 45 and following the same procedure as that described for the pyridazine series. The independent symmetry coordinates (S_2) and the redundancy relationships are given in Tables IIIS and IVS, respectively.

Thus, to make the transformation in eq 2 possible, the symmetry force constants of Goodman et al.[43] expressed in terms of Whiffen's coordinates[46] (series 1, $\mathbf{U}_1$) were transformed to Duinker's in-plane symmetry coordinate set (series 2) by using eq 1 and to the out-of-plane symmetry coordinates set defined in the present work by using the relation

$$F_{S_2} = \mathbf{T}^T F_{S_1} \mathbf{T} \qquad (3)$$

where F_{S_2} and F_{S_1} are the force constant matrices expressed in terms of the ISC sets defined in the present work (series 2) and those in terms of the coordinate set used by Goodman et al. (series 1), respectively; $\mathbf{T}$ is the matrix defined as $(\mathbf{B}_1\mathbf{B}_2{}')$ in ref 10. This transformation was accomplished by using the VIBRA program.[36]

(2) The force fields of each reference molecule in terms of VICs in canonical form ($F_R{}^*$) were transferred to the *target molecule*, setting up the relation between the simple valence force constants of both molecules (the reference and target molecules). Then, the resulting $F_R{}^*$ force fields of the target molecule were transformed to ISCs to carry out the refinement procedure. This transformation was performed by using the relation[3,4b,10]

$$F_S = \mathbf{W} F_R{}^* \mathbf{W}^T \qquad (4)$$

The resulting values for the force constants, after the coordinate transformations from the three series of potentials, are shown (a) for pyridazine in Tables VS−VIIIS for A_1, B_2, A_2, and B_1 symmetry species, respectively, and (b) for 3,6-dichloropyridazine in Tables IXS−XIIS for A_1, B_2, A_2, and B_1 symmetry species, respectively.

II.4. Refinement Details. In all of the cases, a linear least-squares procedure was performed to refine the initial force fields by using the ASYM40 program.[47] Two different criteria of uncertainties associated with each of the observed data points were tested. First, when the vibration wavenumber errors were assigned in proportion to their magnitude (i.e., taking $\mathbf{W}_{\lambda i}$ proportional to $1/\lambda_i$),[2,48] an uncertainty of 1% of the observed wavenumbers was used. Second, all of the wavenumbers were assigned the same uncertainty[49] (1 cm^{-1} corresponding to the experimental error). Finally, the former option was adopted because the discrepancies between the calculated ω and the observed ν wavenumbers undoubtedly arose largely from anharmonicity and the analysis assumed that these errors were larger for the higher wavenumbers. However, with the second criterion, the analysis assumed that these errors were randomly distributed. This inevitably weighted the lower wavenumbers

TABLE 4: Root-Mean-Square (rms) Deviations in cm^{-1} between Experimental and Calculated Wavenumbers of the Pyridazine Isotopomers[a]

	pyridazine-h_4	pyridazine-$3,6$-d_2	pyridazine-d_4	total
		A_1 Symmetry		
MP2/6-311G**	3.5	6.3	4.6	4.7
HF/6-31G*	6.7	5.3	6.6	6.3
BLYP/6-31G*	4.2	5.0	4.7	4.6
B3LYP/6-31G*(scaled)	3.2	5.5	6.3	5.0
transferred from benzene	7.1	8.6	11.9	9.2
		B_2 Symmetry		
MP2/6-311G**	5.5	5.2	4.6	5.2
HF/6-31G*	4.5	5.4	4.3	4.7
BLYP/6-31G*	3.9	4.2	3.0	3.8
B3LYP/6-31G*(scaled)	3.6	3.9	2.9	3.5
transferred from benzene	13.0	8.6	13.3	11.9
		A_2 Symmetry		
MP2/6-311G**	4.5	9.1	12.2	8.7
HF/6-31G*	5.9	26.3	18.3	18.9
BLYP/6-31G*	11.9	19.0	15.2	15.7
B3LYP/6-31G*(scaled)	11.6	17.6	13.9	14.6
transferred from benzene	5.5	6.3	12.9	8.3
		B_1 Symmetry		
MP2/6-311G**	5.9	6.4	2.5	5.3
HF/6-31G*	8.0	9.9	2.9	7.6
BLYP/6-31G*	2.8	2.6	2.1	2.6
B3LYP/6-31G*(scaled)	4.3	4.5	2.1	3.8
transferred from benzene	3.0	2.2	1.5	2.5

[a] The rms deviations of the calculated fundamentals from the different refinement procedures were defined by rms = $[\sum_i(\omega_i^{theor} - \nu_i^{expt})^2/N]^{1/2}$ where ω_i^{theor} and ν_i^{expt} are the ith theoretical harmonic and ith experimental fundamental wavenumbers (in cm^{-1}), respectively, and N denotes the number of normal modes.

TABLE 5: Root-Mean-Square (rms) Deviations in cm^{-1} between Experimental and Calculated Wavenumbers of 3,6-Dichloropyridazine[a,b]

	A_1 symmetry	B_2 symmetry
MP2/6-311G**	3.5	5.6
HF/6-31G*	27.0	0.7
BLYP/6-31G*	2.6	7.3
B3LYP/6-31G*(scaled)	2.2	2.4
transferred from pyridazine		
(A)[c]	38.9	3.4
(B)[d]	47.1	13.2

[a] See footnote a of Table 3 for the definition of the rms. [b] Wavenumbers selected from ref 23 in Table 2. [c] (A) from a force field transferred from benzene.[43] [d] (B) from a MP2/6-311G** ab initio force field.

less than the higher ones, with a consequent slightly poorer precision of the force constants associated with bending and skeletal deformational motions.

In general, the total number of refining parameters (m) was smaller than the total number of observed data (n). However, in some symmetry blocks related to the force fields transferred from benzene, it was necessary, as an exceptional measure, to fit $n = m$.

III. Discussion and Analysis of the Results

III.1. Fitting to the Observed Data. The root-mean-square (rms) deviations between experimental and calculated wavenumbers for pyridazine and its chlorinated derivative are shown in Tables 4 and 5, respectively (rms is defined in the footnote of Table 4).

For in-plane vibrations, the best fit to the experimental wavenumbers of pyridazine as well as to 3,6-dichloropyridazine was obtained with the BLYP/6-31G*, B3LYP/6-31G*(scaled), and MP2/6-31G* potentials, where rms has values on the order of 5.0−2.0 cm^{-1}. By contrast, the worst rms values were

obtained with the transferred force fields (i.e., those from the transfers benzene ⟹ pyridazine and pyridazine ⟹ 3,6-dichloropyridazine). In addition, for the chlorinated derivative, the fit of the HF/6-31G* force field is not satisfactory either. The largest rms value was for the A_1 symmetry block of 3,6-dichloropyridazine with values on the order of 40.0 and 27.0 cm^{-1} with the transferred and the HF/6-31G* potentials, respectively. Because there were force fields that provided a good fit to the experimental data, we rejected a possible problem of misassignment and, in our opinion, these large deviations could be due to the fact that only a reduced number of force constants (eight) are refined in a block of a 9 × 9 dimension. It is usual in a problematic fitting procedure like this that the fundamental wavenumbers depend simultaneously on several diagonal and off-diagonal force constants.

The out-of-plane fundamentals of pyridazine, and especially those with the A_2 symmetry, show poorer fits than do those of the in-plane vibrations. The force field MP2/6-311G* and that transferred from benzene produce wavenumbers nearest to the experimental ones with a total rms of 8.7 and 8.3 cm^{-1}, respectively. In addition, for the B_1 fundamentals, it is observed that the fittings are quite good with the rms values small and of the same order for the three isotopomers. Thus, the five tested force fields, except the HF/6-31G*, give rms values on the order of 2.5 cm^{-1}. Globally, for the normal modes of the out-of-plane vibrations, the MP2/6-311G** and the transferred-from-benzene force fields give the best and the most regular behavior for both symmetry species.

For the out-of-plane vibrations of 3,6-dichloropyridazine, in all of the cases except for the A_2 block of the BLYP/6-31G* potential, we solved a set of simultaneous linear equations rather than performing a least-squares calculation. In the refined A_2 block, the ν_{10}, ν_{11}, ν_{12}, and ν_{13} fundamentals with experimental wavenumbers of 983, 741, 408, and 299 cm^{-1} are calculated as 995, 752, 405, and 292 cm^{-1}. This gives an rms value of 9.8 cm^{-1}.

TABLE 6: Calculated and Refined Values and Uncertainties of the Force Constants of A_1 Symmetry of Pyridazine and 3,6-Dichloropyridazine[a-c]

| | pyridazine | | | | | | 3,6-dichloropyridazine | | | | | |
| | MP2/6-311G** | | | B3LYP/6-31G*(scaled) | | | MP2/6-311G** | | | B3LYP/6-31G*(scaled) | | |
	initial	refined	$\sigma\{F\}$	initial	refined	$\sigma\{F\}$	initial	refined	$\sigma\{F\}$	initial	refined	$\sigma\{F\}$
$F_{1,1}$	5.688	5.203	0.046	5.164	5.199	0.044	4.217	4.018	0.179	3.864	3.836	0.110
$F_{1,2}$	0.005			0.008			0.002			0.005		
$F_{2,2}$	5.728	5.149	0.046	5.203	5.157	0.043	5.768	5.206	0.108	5.292	5.215	0.011
$F_{3,1}$	0.161	−0.306	0.174	0.208	−0.246	0.090	0.552			0.650		
$F_{3,2}$	−0.013			0.001			−0.014			−0.004		
$F_{3,3}$	6.489	5.113	0.126	5.963	5.957	0.139	6.355	5.347	3.151	6.050	6.296	0.054
$F_{4,1}$	0.052			0.079			0.318			0.353		
$F_{4,2}$	0.018			0.048			0			0.033		
$F_{4,3}$	1.487	1.426	0.059	1.712	1.637	0.202	1.362			1.599		
$F_{4,4}$	6.134	6.112	0.226	5.452	5.421	0.216	6.141	5.884	3.137	5.298		
$F_{5,1}$	−0.057			−0.040			−0.011			−0.013		
$F_{5,2}$	0			0.016			−0.012			0.001		
$F_{5,3}$	0.487	0.941	0.087	0.778	0.801	0.107	0.383			0.686		
$F_{5,4}$	0.015			−0.168			0.040			−0.168		
$F_{5,5}$	5.701	5.517	0.237	5.444	5.345	0.199	5.605	5.605	4.998	5.309	5.060	0.090
$F_{6,1}$	−0.005			−0.009			−0.035			−0.039		
$F_{6,2}$	0.079			0.122			0.071			0.112		
$F_{6,3}$	0.065			−0.063			0.152			0.018		
$F_{6,4}$	0.226			0.349			0.206			0.353		
$F_{6,5}$	1.356	1.528	0.094	1.404	1.589	0.088	1.396			1.451		
$F_{6,6}$	6.442	1.476	0.164	6.007	6.276	0.056	6.521	6.408	0.055	6.099	6.157	0.034
$F_{7,1}$	0.126			0.114			0.497			0.484		
$F_{7,2}$	−0.064			−0.065			−0.056			−0.043		
$F_{7,3}$	−0.202			−0.172			−0.122			−0.110		
$F_{7,4}$	−0.032			−0.485			0.062			0.087		
$F_{7,5}$	0.541			0.514			1.014			1.012		
$F_{7,6}$	0.316	0.445	0.091	0.302	0.369	0.063	2.439			2.286		
$F_{7,7}$	1.454			1.436	1.471	0.013	2.391			2.307		
$F_{8,1}$	0.023			0.010			−0.009			−0.004		
$F_{8,2}$	0.004			0.004			−0.015			−0.013		
$F_{8,3}$	−0.237	0.383	0.084	−0.222	0.400	0.083	−0.036			−0.359		
$F_{8,4}$	0.137	−0.205	0.022	0.132	−0.209	0.028	0.258			0.244		
$F_{8,5}$	−0.039			−0.028			0.004			0.011		
$F_{8,6}$	0.014			0.008			−0.034			−0.028		
$F_{8,7}$	−0.054			−0.055			−0.102			−0.106		
$F_{8,8}$	0.573	0.541	0.007	0.551	0.549	0.006	0.942	0.982	0.046	0.941	1.007	0.025
$F_{9,1}$	0.010			0.010			0.023			0.020		
$F_{9,2}$	−0.020			−0.019			−0.003			0.003		
$F_{9,3}$	−0.025			−0.016			−0.039			−0.027		
$F_{9,4}$	−0.147			−0.138			−0.187			−0.169		
$F_{9,5}$	0.073			0.059			0.071			0.055		
$F_{9,6}$	0.216			0.196			0.231			0.208		
$F_{9,7}$	0.122			0.112			0.178			0.162		
$F_{9,8}$	0.020			0.019			0.009			0.013		
$F_{9,9}$	0.484	0.444	0.010	0.464	0.438	0.008	0.525	0.483	0.086	0.498	0.497	0.006

[a] Calculated force constants are referred to as initial. Unrefined force constants were fixed to their initial values. [b] Twenty-two and nine experimental data points for pyridazine and 3,6-dichloropyridazine, respectively, were used in the refinement procedure. [c] Force constants are in units of aJ Å^{-2}.

Thus, it can be concluded that the MP2/6-311G**, B3LYP/6-31G*(scaled), and BLYP/6-31G* potentials show the most regular behavior through the pyridazine series. The force field transferred from benzene has a reasonable response for the in-plane vibrations of pyridazine and is particularly accurate on the out-of-plane vibrations of this parent molecule. The force fields transferred to the chlorinated derivative give very variable results, basically because of the limited number of experimental data to be used as a reference in the fitting process.

III.2. Force Constants in Terms of Symmetry Coordinates. In the tables and the discussion, we considered only the force fields which gave the most satisfactory rms results between the calculated and the experimental wavenumbers (previous section) as well as the lowest uncertainties of the refined symmetry force constants (i.e., MP2/6-311G** and B3LYP/6-31G*(scaled) potentials). Some other potentials will be included in the discussion, for example, the force fields transferred from

benzene for the A_2 vibrations of pyridazine, making further analysis possible. The force constants which were not refined were constrained to their initial values. Next we discuss the details of the results.

In-Plane Vibrations. The force constants of pyridazine and 3,6-dichloropyridazine, which belong to the A_1 symmetry, are shown in Table 6 and those of the B_2 symmetry in Table 7. For pyridazine, all of the diagonal and 13 of the interaction force constants along with 7 of the A_1 symmetry and 6 of the B_2 species were refined. The selected off-diagonal parameters were those that showed the most influence on the calculated wavenumbers. For 3,6-dichloropyridazine, all of the diagonal force constants except $F_{7,7}$ and $F_{22,22}$ were refined.

It is observed (Tables 6 and 7) that the $F_{1,1}$, $F_{2,2}$, $F_{6,6}$, $F_{7,7}$, $F_{8,8}$, $F_{9,9}$, $F_{17,17}$, $F_{18,18}$, $F_{23,23}$, and $F_{24,24}$ force constants of pyridazine reach similar values with any of the initial potentials considered and that they show the lowest uncertainties. The

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TABLE 7: Calculated and Refined Values and Uncertainties of the Force Constants of B_2 Symmetry of Pyridazine and 3,6-Dichloropyridazine[a]

	pyridazine						3,6-dichloropyridazine					
	MP2/6-311G**			B3LYP/6-31G*(scaled)			MP2/6-311G**			B3LYP/6-31G*(scaled)		
	initial	refined	$\sigma\{F\}$	unitial	refined	$\sigma\{F\}$	initial	refined	$\sigma\{F\}$	initial	refined	$\sigma\{F\}$
$F_{17,17}$	5.687	5.260	0.036	5.161	5.227	0.025	4.143	3.764	0.169	3.764	3.804	0.116
$F_{18,17}$	0.006			0.007			−0.005			-0.003		
$F_{18,18}$	5.716	5.144	0.038	5.187	5.147	0.027	5.759	5.190	0.155	5.280	5.191	0.021
$F_{19,17}$	0.169	0.663	0.451	0.188	0.258	0.176	0.625			0.734		
$F_{19,18}$	−0.023			−0.318			−0.021			-0.029		
$F_{19,19}$	6.339	6.573	0.230	6.171	6.476	0.137	6.250	6.777	0.492	6.295	6.817	0.263
$F_{20,17}$	0.083			0.103			0.452			0.468		
$F_{20,18}$	0.061			0.089			0.034			0.062		
$F_{20,19}$	−0.984	−1.071	0.055	−0.869	-0.890	0.035	−1.000			−0.862		
$F_{20,20}$	5.743	5.159	0.134	5.301	5.074	0.112	5.689	4.662	0.596	5.114	4.754	0.337
$F_{21,17}$	−0.086			−0.064			−0.216			−0.175		
$F_{21,18}$	0.013			0.013			0.022			0.024		
$F_{21,19}$	−0.469	−0.953	0.074	−0.511	−0.721	0.056	−0.581			−0.657		
$F_{21,20}$	0.259	0.333	0.046	0.254	0.242	0.026	0.180			0.171		
$F_{21,21}$	1.385	1.397	0.229	1.332	1.387	0.176	1.266	1.223	0.077	1.188	1.242	0.053
$F_{22,17}$	−0.098			−0.101			−0.346			−0.324		
$F_{22,18}$	0.174			0.165			0.152			0.143		
$F_{22,19}$	0.124			0.113			0.117			0.091		
$F_{22,20}$	−0.227	−0.074	0.049	−0.197	−0.119	0.047	−0.189			−0.157		
$F_{22,21}$	0.054			0.032			0.072			0.048		
$F_{22,22}$	1.291	1.315	0.257	1.264	1.266	0.169	1.237			1.213		
$F_{23,17}$	0.024			0.014			0.018			0.023		
$F_{23,18}$	−0.011			−0.009			−0.023			−0.031		
$F_{23,19}$	−0.342	−0.293	0.017	−0.314	−0.293	0.012	−0.434			−0.428		
$F_{23,20}$	0.149			0.132			0.163			0.140		
$F_{23,21}$	0.106			0.098			0.093			0.083		
$F_{23,22}$	−0.059			−0.049			−0.023			−0.015		
$F_{23,23}$	0.563	0.548	0.009	0.543	0.548	0.007	0.916	0.909	0.031	0.924	0.902	0.034
$F_{24,17}$	−0.007			−0.004			−0.003			−0.009		
$F_{24,18}$	−0.002			0.001			0.013			0.020		
$F_{24,19}$	0.064			0.053			0.047			0.039		
$F_{24,20}$	−0.134			−0.117			−0.185			−0.159		
$F_{24,21}$	−0.060			−0.054			−0.005			−0.048		
$F_{24,22}$	0.039			0.038			0.035			0.035		
$F_{24,23}$	−0.004			−0.003			−0.023			−0.015		
$F_{24,24}$	0.504	0.489	0.007	0.484	0.486	0.004	0.539	0.529	0.023	0.511	0.508	0.009

[a] Calculated force constants are referred to as initial. Unrefined force constants were fixed to their initial values. [b] Twenty and eight experimental data points for pyridazine and 3,6-dichloropyridazine, respectively, were used in the refinement procedure. [c] Force constants are in units of aJ Å^{-2}.

remaining diagonal force constants of pyridazine associated with the ring-stretching and ring-deformation movements give more variable values depending on the force field, and they are also calculated with higher uncertainties. For 3,6-dichloropyridazine, the behavior is similar, but the uncertainties of the force constants related to the ring displacements are larger than those in the parent molecule.

When the A_1 and B_2 symmetry blocks of pyridazine are compared, it can be observed that the refined diagonal force constants of B_2 symmetry present more uniform values than those in the A_1 block. The uncertainties also turned out to be smaller with values on the order of 0.007 aJ Å^{-2} for $F_{23,23}$ and $F_{24,24}$.

The off-diagonal parameters obtained with the quantum mechanical and scaled force fields present the same sign after being refined.

Out-of-Plane Vibrations. The force constants of pyridazine and 3,6-dichloropyridazine, which belong to the A_2 and B_1 symmetry species, are shown in Table 8.

For pyridazine, all of the diagonal force constants were refined in the two symmetry blocks. In Table 8, it can be observed that the diagonal force constants present similar values for the various force fields tested. All of the force constants show quite small uncertainties which are of the same order of magnitude

from the various force fields analyzed. In particular, the lowest uncertainties are obtained in the B_1 symmetry force constants with values that are several orders of magnitude smaller than those of the associated force constants.

Although, in general, the worst fitting between the calculated and experimental wavenumbers was obtained for the A_2 symmetry block, an exception is the force field transferred from benzene, where the rms values are 5.5, 6.3, and 12.9 cm^{-1} for the h_4, $3,6$-d_2, and d_4 species, respectively (see Table 4). In particular, it was observed (Table 8) that, for this force field, the diagonal and the interaction $F_{12,10}$ force constants were the most sensitive to the observed wavenumbers, while for the other force fields, the nine force constants of the block played an equally decisive role in the observed data.

For 3,6-dichloropyridazine, we solved the set of simultaneous linear equations, rather than performing a least-squares calculation (noted as "direct calculation" in Table 8). Thus, all of the diagonal constants were calculated from the experimental wavenumbers, keeping the interaction force constants fixed to the calculated initial values. For the B_1 symmetry force fields, all of the potentials gave similar values with such results being more systematic than those in the A_2 symmetry species, where the most significant discrepancy is shown by the $F_{10,10}$ force constant which is associated with the most complicated sym-

TABLE 8: Calculated and Refined Values and Uncertainties of the Pyridazine and 3,6-Dichloropyridazine Force Constants of A$_2$ and B$_1$ Symmetry^a

| | pyridazine^b | | | | | | | | | 3,6-dichloropyridazine | | | |
| | transferred from benzene | | | MP2/6-311G** | | | B3LYP/6-31G*(scaled) | | | MP2/6-311G** | | B3LYP/6-31G*(scaled) | |
	initial	refined	$\sigma\{F\}$	initial	refined	$\sigma\{F\}$	initial	refined	$\sigma\{F\}$	initial	direct calculation^d	initial	direct calculation^d
						A$_2$ Symmetry							
$F_{10,10}$	0.281	0.343	0.013	0.274	0.334	0.012	0.319	0.333	0.022	0.320	0.466	0.363	0.352
$F_{11,10}$	0.012			0.050			0.012			0.066		0.025	
$F_{11,11}$	0.291	0.318	0.009	0.230	0.266	0.009	0.298	0.267	0.013	0.234	0.287	0.288	0.252
$F_{12,10}$	−0.022	0.084	0.019	0.053			0.045			0.072		0.065	
$F_{12,11}$	−0.009			0.017			0.017			0.011		0.012	
$F_{12,12}$	0.337	0.287	0.016	0.195	0.274	0.015	0.211	0.301	0.036	0.199	0.208	0.208	0.211
$F_{13,10}$	0.038			0.018			0.042			0.005		0.029	
$F_{13,11}$	−0.060			−0.024			−0.052			−0.006		−0.22	
$F_{13,12}$	−0.039			−0.037			−0.038			−0.007		−0.007	
$F_{13,13}$	0.368	0.218	0.017	0.331	0.252	0.021	0.352	0.211	0.029	0.315	0.270	0.322	0.399
						B$_1$ Symmetry							
$F_{14,14}$	0.298	0.312	0.005	0.277	0.308	0.008	0.296	0.311	0.006	0.320	0.308	0.335	0.303
$F_{15,14}$	−0.004			0.011			0.004						
$F_{15,15}$	0.298	0.298	0.003	0.301	0.281	0.006	0.313	0.287	0.005	0.307	0.313	0.314	0.308
$F_{16,14}$	0.049	0.006	0.003	−0.008			−0.003						
$F_{16,15}$	−0.024			−0.021			−0.025						
$F_{16,16}$	0.311	0.219	0.002	0.222	0.227	0.003	0.232	0.223	0.002	0.186	0.309	0.192	0.316

^{a} Calculated force constants are referred to as initial. Unrefined force constants were fixed to their initial values. ^{b} Eight and seven experimental data points for A$_2$ and B$_1$ symmetry species, respectively, were used in the refinement procedure. ^{c} Force constants are in units of aJ Å^{-2}. ^{d} See text for a description.

TABLE 9: Canonical Ring-Stretching and CH and CCl Deformation Force Constants of Pyridazine and 3,6-Dichloropyridazine in Terms of Simple VICs^{a,b}

| | pyridazine | | | | 3,6-dichloropyridazine | | | |
| | MP2/6-311G** | | B3LYP/6-31G*(scaled) | | MP2/6-311G** | | B3LYP/6-31G*(scaled) | |
force constants	initial	refined	initial	refined	initial	refined	initial	refined
$f_{1\text{(NN stretch)}}$	4.964	4.725	4.657	4.565	4.893	5.227	4.547	4.332
$f_{2\text{(NC stretch)}}$	5.667	5.113	5.349	5.472	5.560	5.298	5.433	5.763
$f_{3\text{(ortho CC stretch)}}$	5.519	5.298	5.011	4.928	5.492	4.986	4.858	4.732
$f_{4\text{(meta CC stretch)}}$	5.999	5.897	5.597	5.869	6.081	5.984	5.689	5.735
$f_{10\text{(ortho CH bend)}}{}^c$	0.568	0.544	0.547	0.549	0.929	0.946	0.932	0.854
$f_{11\text{(meta CH bend)}}$	0.494	0.466	0.474	0.462	0.532	0.506	0.504	0.502

^{a} Force constants in units of aJ Å^{-2}. ^{b} The ortho and meta positions are defined with respect to the CN bond. ^{c} Ortho CCl bend for 3,6-dichloropyridazine.

metry coordinate of this species (which includes a linear combination of all of the out-of-plane internal coordinates; Table 1).

III.3. Force Constants in Terms of VICs in Canonical Form. The symmetry force constants were expressed in terms of VICs in canonical form. The goals of this transformation were, in the work described in previous sections, to accomplish the transference procedures between related molecules and, in the present section, to analyze the physicochemical meaning of the force constants in VICs. The complete numerical results are available as Supporting Information (Tables XIIIS and XIVS for pyridazine and Tables XVS and XVIS for 3,6-dichloropyridazine). In this section, using the 111 and 31 force constants in VICs for the in-plane and out-of-plane vibrations, respectively, we consider the physicochemical significance of the most interesting force constants in terms of the previously mentioned canonical internal coordinate system. Also, we refer only to those force fields which gave the best fits to the experimental data and the smallest uncertainties for the refined symmetry force constants [i.e., MP2/6-311G** and B3LYP/6-31G*(scaled) potentials]. Some other potentials, which are interesting for a comparative study, for example, the force fields transferred from benzene, are also mentioned in the discussion.

In-Plane Canonical Force Constants. Considering the ring-stretching force constants (i.e., f_1, f_2, f_3, and f_4 of pyridazine and 3,6-dichloropyridazine), it can be seen in Table 9 that the NN stretching force constant (f_1) is smaller than the other ring stretching force constants. The constant f_2 (CN stretching) is larger than f_3 (ortho CC stretching, with respect to the CN bond) and smaller than f_4 (meta CC stretching, with respect to the CN bond). After the refinement, we observe the following tendency: $f_1 < f_2$ and $f_3 < f_4$. This systematic behavior, observed in pyridazine as well as 3,6-dichloropyridazine, can be due to the fact, proved a long time ago[50] and easily checked by the Hückel molecular orbital method,[51] that pyridazine shows an alternation of bond orders in contrast with, for instance, pyridine, pyrimidine, pyrazine, and s-triazine.[52] This indicates that the electronic structure of this molecule is shifted from the aromatic structure toward the Kekulé structure, which has double bonds between the C and N atoms and in the CC meta bond. However, in pyridine, pyrimidine, pyrazine, and s-triazine, the two possible Kekulé structures are topologically equivalent, so they both contribute with the same weight, giving similar orders to the bonds. In particular, spin-coupled theory, when applied to the π electrons of benzene and the heteroaromatic molecules (pyridine, pyridazine, pyrimidine, and pyrazine), obtained the result[53] for pyridazine where the Kekulé structure with a singlet coupling of π electrons on the adjacent nitrogen atoms contributed 20.5%, whereas the other Kekulé form had an occupation number of 54%. On the other hand, the remaining

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TABLE 10: Aromaticity Indices for Azines

compound	RCI[b]	RE (MP3/6-31G**//6-31G*)[a]	ΔH_{diss}[a] calc[c]	ΔH_{diss}[a] obs
benzene	1.751	36.0	153	143
pyridine	1.731	34.2	117	105
pyrazine	1.739	32.0	74	70
pyrimidine	1.727	32.6	78	70
pyridazine	1.716	26.1	50	50

[a] Resonance energy (RE) calculated from the energies of hydrogen-transfer reactions; RE and ΔH_{diss} are in kcal/mol.[55] [b] Ring current index (RCI; Jug, K. *J. Org. Chem.* **1993**, *48*, 1344). [c] Based on MP3/6-31G**//6-31G* energy changes.

three Dewar structures contributed ca. 8.5% each. All of this evidence points to a low aromatic character of the pyridazine ring, especially as compared with the other azines.[52] The structural indices of aromaticity listed in Table 10 indicate, as a rule, the same trends in the estimation of aromaticity of the azine series.[54] The aromaticity of azines, and especially of pyridazine, is reduced relative to benzene, as is evidenced by the ring current index (RCI) values (Table 10) as well as by the resonance energies (RE) values calculated from the energies of hydrogen-transfer reactions. The relatively low RE values of pyridazine compared to those of benzene are explained primarily by changes in the σ system that occur in passing from the conjugated system to the reference system (i.e., by factors such as the compression energy that are included in the so-called empirical resonance energies). Another factor that may be responsible for the lower resonance energy of pyridazine is the difference in bond energy between σ bonds involving the NN group in the azine and its reduced form.[55] To support these arguments, calculated and observed data of dissociation enthalpies for benzene and the azine series are included in Table 10.

Considering the numerical values of the force constants, it can be seen in Table 9 for pyridazine and its dichlorinated derivative that f_1 has significantly lower values than those for a typical N=N stretching (10.347 aJ Å^{-2});[56] on the other hand, f_2 presents values significantly larger than those of a CN single bond (3.756 aJ Å^{-2}).[56] Finally, the CC stretching force constants (f_3 and f_4) are both larger than the CC stretching force constant in benzene (4.892 aJ Å^{-2}),[43] especially f_4, as should be expected.

With the force field transferred from benzene (not included in Table 9), we observe the tendency $f_1 > f_2$ and $f_3 > f_4$, which disagrees with the considerations explained above. This contradictory result may be due to the fact that the same value for the stretching force constants of the entire starting ring was considered in the initial force field. Such a value corresponds to the CC bond stretching value of the prototypical benzene aromatic structure. Both would lead to contradictory results.

With relation to the CH and CCl stretching force constants, f_5 (f_{CH} ortho with respect to the NC bond and f_{CCl} for 3,6-dichloropyridazine) and f_6 (f_{CH} meta with respect to the NC bond), the initial force fields for the parent molecule give $f_6 > f_5$ (Table XIIIS). However, after the refinement, f_6 is slightly smaller than f_5. For pyridazine, the former presents values in the range of 5.146–5.152 aJ Å^{-2} and the latter between 5.231 and 5.213 aJ Å^{-2}. In comparative studies of force constants relative to CH displacements, difficulties appear when the values to be compared have been calculated, on the one hand, from harmonic wavenumbers and, on the other hand, from anharmonic wavenumbers. Thus, in the present work, we have used anharmonic wavenumbers, whereas harmonic frequencies were used for benzene by Goodman et al.[43] However, we should mention that both series of values mentioned above are smaller than the CH stretching force constant of benzene (5.547 aJ Å^{-2}).

With respect to the relation $f_6 < f_5$, this is a contradictory result. We expected to find the meta CH bond stronger than that in the ortho position because, in the last case, the proximity of the N atom, more electronegative than C, would be expected to distort the electron density of the CH bond, weakening the bond and making the associated stretching force constant smaller.

The CCl and CH stretching force constants of 3,6-dichloropyridazine (f_5 and f_6) were calculated with values between 3.820 and 3.891 aJ Å^{-2} for the former and between 5.198 and 5.203 aJ Å^{-2} for the latter. The constant f_6 has values between those observed for f_6 and f_5 in pyridazine. When the values of f_5 are compared qualitatively with those for the CCl stretching force constants in o-, m-, and p-dichlorobenzene[57] (3.817, 3.717, and 3.713 aJ Å^{-2}, respectively), it is observed that the interval where f_5 is calculated is closest to the value of the force constant of o-dichlorobenzene, which does not present the same relative position as the Cl atoms in dichloropyridazine.

The force constants corresponding to the CH (CCl in 3,6-dichloropyridazine) deformation ortho (f_{10}) and meta (f_{11}) with respect to the CN bond are shown in Table 9. The theoretical and scaled force fields predict f_{10} to be larger than f_{11}. This tendency continues after the refinement. While the higher electronegativity of the nitrogen atom should deform the electron density of the ortho CH bond of pyridazine during the bending movement, the above tendency could be due to the repulsive interaction between the electron density of the hydrogen atom and the lone pair electrons of the nitrogen, which causes the associated bending force constant to be larger than those associated with the meta CH bond. For this latter bond, the lone pair electrons of nitrogen are far from the hydrogen atom. For the dichlorinated derivative, the two force fields predict f_{10} to be significantly larger than f_{11}. This behavior can be explained by considering that the electron density of the voluminous chlorine atom interacts with the lone pair electrons of the nitrogen atoms during the bending movement. This tendency continues after the refinement with values for f_{10} between 0.854 and 0.946 aJ Å^{-2} and for f_{11} between 0.502 and 0.506 aJ Å^{-2}. The results are supported by comparing f_{10} and f_{11} in pyridazine and 3,6-dichloropyridazine; in the latter molecule, the difference between the constants is larger because the interaction of the electron density of the Cl atom with the lone pair electrons of the nitrogen atoms is also larger than that between the electron density of the hydrogen atom and the same lone pair electrons in pyridazine.

With respect to the interaction force constants, it is noteworthy that the values of the NN stretching−para CC stretching force constant (f_{14}) are on the order of 2.070 and 1.930 aJ Å^{-2} for pyridazine and 3,6-dichloropyridazine, respectively, after refinement. These values are larger than those of the bond stretching and CH and CCl deformation diagonal force constants. A similar situation has been observed in benzene,[43] where the para CC interaction force constants gave a value of 2.107 aJ Å^{-2}, whereas the diagonal force constants for CC and CH bending were 1.369 and 0.993 aJ Å^{-2}, respectively. Just as with f_{14}, the CN stretching−para CC stretching interaction force constant (f_{17}) shows high values, even larger than those for the diagonal force constants of ring and CH and CCl deformations. Thus, f_{17} gives values ranging between 1.834 and 2.111 aJ Å^{-2} for pyridazine and in the interval between 1.808 and 1.893 aJ Å^{-2} for 3,6-dichloropyridazine.

In general, the ortho and meta ring-stretching interaction force constants gave values significantly smaller than those of f_4 and f_5, and they are always positive (Tables XIIIS and XVS) except

TABLE 11: Canonical Torsion Force Constants of Pyridazine and 3,6-Dichloropyridazine in Terms of Simple VICs[a,b]

	pyridazine				3,6-dichloropyridazine			
	MP2/6-311G**		B3LYP/6-31G*(scaled)		MP2/6-311G**		B3LYP/6-31G*(scaled)	
force constants	initial	refined	intial	refined	initial	refined	initial	refined
$f_{3'}$(NN torsion)	0.097	0.139	0.108	0.153	0.097	0.109	0.103	0.103
$f_{4'}$(NC torsion)	0.147	0.159	0.151	0.163	0.132	0.165	0.135	0.169
$f_{5'}$(ortho CC torsion)	0.154	0.134	0.161	0.121	0.142	0.162	0.144	0.194
$f_{6'}$(meta CC torsion)	0.169	0.145	0.179	0.127	0.176	0.167	0.182	0.212

[a] Force constants are in units of aJ Å^{-2}. [b] The ortho and meta positions were defined with respect to the CN bond.

for f_{15} (the CN stretching−ortho CC stretching interaction force constant) and f_{18} (the CN stretching−CN stretching interaction force constant) whose values are negative with the MP2/6-311G** and B3LYP/6-31G* force fields.

The rest of the interaction force constants give, in most cases, similar values (sign and magnitude) with the various force fields tested. In general, the force constants with the most variable predicted signs correspond to those of small magnitude, while by contrast, other more significant values agree in sign when calculated from the various initial force fields.

Out-of-Plane Canonical Force Constants. The CH and CCl wagging force constants of pyridazine and 3,6-dichloropyridazine (f_1' and f_2') are shown in Tables XIVS and XVIS. All of the force fields predicted f_1' to be larger than f_2'. In particular, for pyridazine, the nonempirical force fields gave f_1' as approximately 0.015 aJ Å^{-2} larger than f_2'. After the refinement, this difference was increased to approximately 0.040 aJ Å^{-2}. Specifically, for the two nonempirical force fields considered, the value of f_1' is 0.295 aJ Å^{-2} and those of f_2' are between 0.261 and 0.240 aJ Å^{-2}. These results are similar to those obtained for tetrazine,[58] where the CH wagging force constant was 0.264 aJ Å^{-2}.

The torsion force constants f_3', f_4', f_5', and f_6' are shown in Table 11. Their values predicted from the theoretical and scaled force fields are smaller than those obtained in benzene[59] for the CC torsion force constant (0.335 aJ Å^{-2}). Moreover, for pyridazine, it can be seen that $f_3' < f_5' < f_6' < f_4'$ [i.e., the NN torsion force constant (f_3') is the smallest, the CN torsion force constant (f_4') is the largest, and the ortho CC torsion force constant (f_5') is smaller than the meta CC torsion force constant (f_6')]. This behavior agrees with that observed in the ring-stretching force constants. In that discussion, it was pointed out that one of the Kekulé structures of this ring is predominant: the one with double bonds located in the CN and meta CC bond. The torsion force constant associated with these bonds would be expected to be larger because the π character of these bonds is also stronger.

For 3,6-dichloropyridazine, the same torsion force constants (i.e., f_3', f_4', f_5', and f_6') were calculated from the theoretical and scaled force fields to have the following tendency: $f_3' < f_4' < f_5' < f_6'$. After the refinement, this tendency was maintained except with the MP2/6-311G** force field where the value for f_4' was almost the same as that for f_5'.

The tendency $f_3' < f_4' < f_5' < f_6'$ disagrees with that found in pyridazine (i.e., $f_3' < f_5' < f_6' < f_4'$). The latter was justified considering the Kekulé structure with the double bond located in the CN and meta CC bond of the ring predominantly; thus, it would be expected that the torsion force constants associated with these bonds would be larger. However, in the chloropyridazine molecule, there is another factor with the opposite effect. That is, the stabilization of the system which results during the torsion when the electron density of the chlorine atoms is localized outside of the molecular plane which contains the sp^2 orbital with the lone pair electrons of the nitrogen atoms.

These two opposite effects can explain the reorganization of the torsion force constants with respect to the values found in pyridazine.

There is agreement in magnitude and sign in most of the interaction force constants from the various initial force fields. Most of these constants are very small as shown in Tables XIVS and XVIS.

IV. Conclusions

Through the **BB**^{T} diagonalization, the redundant relations among the VIC sets defined for our two molecules were obtained. In each case, an ISC set was calculated by an orthonormalization procedure with respect to these redundancy relationships. Force fields in canonical form were used to carry out the force field transference between related molecules (i.e., benzene−pyridazine and pyridazine−3,6-dichloropyridazine).

For these two molecules, the behavior of various initial force fields subjected to an empirical refinement by a least-squares procedure was analyzed. In summary, the B3LYP/6-31G*(scaled) and MP2/6-311G** force fields for the two molecules and the force field transferred from benzene for pyridazine showed the most satisfactory and systematic behavior throughout this series. In general, reliable values were obtained for the diagonal force constants, which showed similar values from the various force fields tested; by contrast, discrepancies appeared with interaction force constants, which also were accompanied, in some cases, by significant uncertainties.

From the most reliable force field in ISCs, it was possible to find physicochemical interpretations of the values of the force constants in terms of VICs in canonical form. In particular, the ring-stretching and torsion force constant values as well as those of the CH and CCl bending force constants were analyzed through the electronic structure of these systems, yielding quite reliable results.

Although the results have not been completely definitive for the pyridazines, significant conclusions have been drawn relative to their force fields. In addition, this study represents a first attempt to explore the potential of the canonical force fields on large molecules and, in particular, cyclic systems. The results point out the broad possibilities of these harmonic canonical potentials. Thus, although limitations have been found with the available experimental information, the resulting force fields in VICs have been shown to reveal physicochemical insight. In addition, the conclusions obtained from this work suggest future research, testing the transference of the force field from benzene to pyridine, as a more favorable example, and from there checking the transferability through all of the azinic series. Also, it would be interesting to explore the evolution of the interesting relations obtained in the present work relative to the aromatic character of the azinic rings and the influence of the inclusion of different halogens in the parent molecules.

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References and Notes

(1) (a) Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular Vibrations. The Theory of Infrared and Raman Vibrational Spectra*; Dover Publications: Mineola, NY, 1955. (b) Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand Reinhold: New York, 1950.

(2) (a) Califano, S. *Vibrational States*; Wiley-Interscience: New York, 1976. (b) Crawford, B., Jr.; Overend, J. *J. Mol. Spectrosc.* **1964**, *121*, 307. (c) Strey, G. *J. Mol. Spectrosc.* **1965**, *17*, 265. (d) Mills, I. M. *Chem. Phys. Lett.* **1969**, *3*, 267. (e) Groner, G.; Günthard, Hs. H. *J. Mol. Spectrosc.* **1976**, *61*, 151.

(3) Kuczera, K.; Czerminski, R. *J. Mol. Struct.* **1983**, *105*, 269.

(4) Gold, R.; Dowling, M.; Meister, A. *J. Mol. Spectrosc.* **1958**, *2*, 9. (b) Kuczera, K. *J. Mol. Struct.* **1987**, *160*, 159. (c) López González, J. J.; Fernández Gómez, M. *J. Mol. Struct.* **1990**, *216*, 297. (d) Fernández Gómez, M.; López, J. J.; Cardenete, A. *J. Mol. Struct.* **1990**, *220*, 287. (e) López González, J. J.; Fernández Gómez, M.; Martínez Torres, E. *J. Mol. Struct.* **1992**, *265*, 397. (f) Fernández Gómez, M.; López González, J. J.; Rajamanickan, N.; Martínez Torres, E. *J. Mol. Struct.* **1992**, *271*, 237. (g) Fenández-Liencres, M. P.; Fernández Gómez, M.; López González, J. J.; Rajamanickam, N. *J. Mol. Struct.* **1997**, *407*, 101. (h) Pupyshev, V. I.; Panchenko, Y. N.; De Maré, G. R.; Bock, C. W. *J. Mol. Struct.* **1992**, *272*, 145.

(5) Pulay, P.; Fogarasi, G. *J. Chem. Phys.* **1992**, *96*, 2856.

(6) Baker, J.; Jarzecki, A. A.; Pulay, P. *J. Phys. Chem.* **1998**, *102A*, 1412.

(7) Baker, J.; Pulay, P. *J. Comput. Chem.* **1998**, *19*, 1187.

(8) Chuang, Y.-Y.; Truhlar, D. G. *J. Phys. Chem.* **1998**, *102A*, 242.

(9) (a) Kuramshina, G. M.; Weinhold, F.; Kochikov, I. V.; Yagola, A. G.; Pentin, Y. A. *J. Chem. Phys.* **1994**, *100*, 1414. (b) Kuramshima, G. M.; Weinhold, F.; Pentin, Y. A. *J. Chem. Phys.* **1998**, *109*, 7286.

(10) Martínez Torres, E.; López González, J. J.; Fernández Gómez, M. *J. Chem. Phys.* **1999**, *110*, 3302.

(11) (a) Rachavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479. (b) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(12) Dunning, T. M. *J. Chem. Phys.* **1989**, *100*, 1007.

(13) Lee, T. L.; Scuseria, G. E. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; p 47.

(14) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley & Sons: New York, 1986.

(15) *Density Functional Methods in Chemistry*; Labanowski, J. H., Andzelm, J. W., Eds.; Springer: New York, 1991.

(16) (a) Rienstra-Kiracofe, J. C.; Graham, D. E.; Schaefer, H. F., III. *Mol. Phys.* **1998**, *94*, 767. (b) Juric, B. S. *Theor. Chim. Acta* **1998**, *99*, 171. (c) Leszczynski, J.; Goodman, L.; Kwiatkowski, J. S. *Theor. Chim. Acta* **1997**, *97*, 195. (d) Jursic, B. S. *J. Mol. Struct. (THEOCHEM)* **1997**, *401*, 45.

(17) Density Functional Theory I. Functionals and Effective Potentials. In *Topics in Current Chemistry*; Nalewajski, R. F., Ed.; Springer: Berlin, 1996; Vol. 180.

(18) Sander, R.; Bettermann, H. *J. Mol. Struct.* **1991**, *263*, 123.

(19) Aldous, J.; Mills, I. M. *Spectrochim. Acta* **1962**, *18*, 1073; **1963**, *19*, 1567.

(20) (a) Gans, P. *Chem. Phys. Lett.* **1970**, *6*, 561. (b) Gans, P. *J. Chem. Soc. A* **1971**, 2017.

(21) (a) Botschwina, P. *Chem. Phys. Lett.* **1974**, *29*, 98; **1974**, *29*, 580. (b) Blom, C. E.; Altona, C. *Mol. Phys.* **1976**, *31*, 1377. (c) Pulay, P.; Fogarasi, G.; Pongor, G.; Boggs, J. E.; Vargha, A. *J. Am. Chem. Soc.* **1983**, *105*, 7073. (d) Rauhut, G.; Pulay, P. *J. Am. Chem. Soc.* **1995**, *117*, 4167.

(22) Vázquez, J.; López González, J. J.; Márquez, F.; Boggs, J. E. *J. Raman Spectrosc.* **1998**, *29*, 547.

(23) Vázquez, J.; López González, J. J.; Márquez, F.; Pongor, G.; Boggs, J. E. *J. Phys. Chem.* **2000**, *104*, 2499.

(24) Kim, H.; Hameka, H. F. *J. Am. Chem. Soc.* **1963**, *85*, 1398.

(25) De la Vega, J. R.; Hameka, H. F. *J. Am. Chem. Soc.* **1963**, *85*, 3504.

(26) Coulson, C. A. *J. Chem. Soc.* **1963**, 5893.

(27) Werner, W.; Dreizler, H.; Rudolph, H. D. *Z. Naturforsh.* **1967**, *22*, 531.

(28) Almenningen, A.; Bjørnsen, G.; Ottersen, T.; Seip, R.; Strand, T. G. *Acta Chem. Scand.* **1977**, *A31*, 63.

(29) Cradock, S.; Purves, Ch.; Rankin, D. W. H. *J. Mol. Struct.* **1990**, *220*, 193.

(30) Blake, A. J.; Rankin, D. W. H. *Acta Crystallogr.* **1991**, *C47*, 1933.

(31) Morrison, C. A.; Smart, B. A.; Parsons, S.; Brown, E. M.; Rankin, D. W. H.; Robertson, H. E.; Miller, J. *J. Chem. Soc., Perkin Trans.* **1997**, *2*, 857.

(32) Harris, D. C.; Bertolucci, M. D. S*ymmetry and Spectroscopy. An Introduction to Vibrational and Electronic Spectroscopy*; Dover Publications: Mineola, NY, 1989.

(33) Hilderbrandt, R. L. *J. Mol. Spectrosc.* **1972**, *44*, 599.

(34) Gussoni, M.; Zerbi, G. *Rend. Accad. Naz. Lincei* **1966**, *40*, 1032.

(35) Collen, Ch. G. *Matrices and Linear Transformations*; Dover Publications: Mineola, NY, 1972.

(36) Martínez Torres, E. *VIBRA*, Version 1.0; Universidad de Castilla-La Mancha: Ciudad Real, Spain, 1997.

(37) *MATHEMATICA; System for Doing Mathematics by Computer*, Version 2.0 for Windows; Wolfarm Research, Inc.: 1991.

(38) Stidham, H. D.; Tucci, J. V. *Spectrochim. Acta* **1967**, *23A*, 2233.

(39) Frisch, M. J.; Truchks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN92*, Revision E.3; Gaussian, Inc.: Pittsburgh, PA, 1992.

(40) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN94*, Revision B.1.; Gaussian, Inc.: Pittsburgh, PA, 1995.

(41) (a) Fogarasi, G.; Pulay, P. Ab Initio Calculation of Force Fields and Vibrational Spectra. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: Amsterdam, 1985; Vol. 14, p 125. (b) Fogarasi, G.; Zhou, X.; Taylor, P. V.; Pulay, P. *J. Am. Chem. Soc.* **1992**, *114*, 819.

(42) Pulay, P.; Fogarasi, G.; Pang, F.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2599.

(43) Goodman, L.; Ozkabak, A. G.; Thakur, S. N. *J. Phys. Chem.* **1991**, *95*, 9044.

(44) Duinker, J. C.; Mills, I. M. *Spectrochim. Acta* **1968**, *24A*, 417.

(45) Langseth, A.; Stoicheff, P. B. *Can. J. Phys.* **1956**, *34*, 350.

(46) Whiffen, D. H. *Philos. Trans. R. Soc. London* **1955**, *248A*, 131.

(47) Hedberg, L.; Mills, I. M. ASYM20-ASYM40, Version 3.0. *J. Mol. Spectrosc.* **2000**, *203*, 82.

(48) Aldous, J.; Mills, I. M. *Spectrochim. Acta* **1962**, *18*, 1073.

(49) Overend, J.; Scherer, J. R. *J. Chem. Phys.* **1960**, *32*, 1720.

(50) Evans, R. C.; Wilselogle, F. Y. *J. Am. Chem. Soc.* **1945**, *67*, 60.

(51) Atkins, P. W.; Friedman, R. S. *Molecular Quantum Mechanics*; Oxford University Press: Oxford, U.K., 1997.

(52) Joule, J. A.; Smith, G. F. *Heterocyclic Chemistry*; Van Nostrand Reinhold: New York, 1987.

(53) Cooper, D. L.; Wright, S. C.; Gerratt, J.; Raimondi, M. *J. Chem. Soc., Perkin Trans. 2* **1989**, 255.

(54) Ya Simkin, B.; Minkin, V. I.; Glukhovtsev, M. N. *Adv. Heterocycl. Chem.* **1993**, *56*, 303.

(55) Wiberg, K. B.; Nakaji, D.; Breneman, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 4178.

(56) López-González, J. J.; Cardenete, A.; Fernández Gómez, M.; Arenas, J. F. *Spectrochim. Acta* **1987**, *43A*, 447.

(57) Zhou, X.; Fogarasi, G.; Liu, R.; Pulay, P. *Spectrochim. Acta* **1993**, *49A*, 1499.

(58) Lorite Villacreces, I.; Fernández Gómez, M.; López González, J. J.; Cardenete Espinosa, A. *Spectrochim. Acta* **1987**, *46A*, 873.

(59) Kydd, R. A. *Spectrochim. Acta* **1971**, *27A*, 2067.

(60) Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry. Introduction to Advanced Electronic Structure Theory*; McGraw-Hill: New York, 1989.

(61) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(62) *Modern Density Functional Theory. A Tool for Chemistry*; Seminario, J. M., Politzer, P., Eds.; Elsevier: Amsterdam, 1995.

(63) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098.

(64) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B41*, 785.

(65) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(66) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(67) *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1991; Vol. 2.

(68) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.