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THEORETICAL FORCE FIELDS AND VIBRATIONAL SPECTRA OF 4H-PYRAN-4-ONE BY CNDO/2 AND MINDO/3 FORCE METHODS

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ABSTRACT

The complete harmonic force fields and the in-plane and out-of-plane vibrational fundamentals of 4H-pyran-4-one are determined by CNDO/2 and MINDO/3 semiempirical quantum chemical methods. The quadratic force constants are scaled using 11 scale factors. In the case of MINDO/3 a standard set of scale factors is used, while in the case of CNDO/2 they are refined. The latter, optimized set of scale factors, is very similar to those published for other molecules. The theoretical vibrational spectra calculated from these scaled quantum mechanical (SQM) force fields are in fair agreement with the experimental gas-phase spectra, confirming the applicability of semiempirical force field calculations for vibrational spectra analysis. The choice of the reference geometry is shown to have only a small effect on the scale factors. Dependence of the scale factors on related geometry parameters is predictable, although other factors (e.g., anharmonic vibrations versus harmonic theoretical treatment) also make important contributions to the final values of the scale factors.

INTRODUCTION

It is quite generally accepted that scaled quantum mechanical (SQM, a term introduced in ref. 1 to imply an a posteriori correction procedure) ab initio force fields can reproduce frequencies of vibrational fundamentals

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within an error of 1—3% [1—10]. The success of this sophisticated procedure has raised questions about the reliability of the results obtained by semiempirical methods. However, these latter methods (e.g., CNDO/2, MINDO/3) are about three orders of magnitude less time-consuming than ab initio methods with a basis set of double-zeta quality. Thus, while speed of calculation may come at the price of less reliability, it was recently shown [9—11] that, using a well-balanced scaling procedure for improving the computed force field (a procedure analogous to that applied to ab initio force fields), these semiempirical calculations can reproduce the experimental frequencies within 5—50 cm^{-1}.

The success of the semiempirical methods inspired us to repeat a recently published ab initio force field calculation for 4H-pyran-4-one [12] on the CNDO/2 and MINDO/3 levels.

In this paper the theoretical vibrational spectra of 4H-pyran-4-one (hereafter γ-pyrone) obtained by SQM CNDO/2 and MINDO/3 harmonic force fields are given. The CNDO/2 optimized scale factors are compared to those obtained for benzene [13], pyridine [14], uracil [15], maleimide [16] and furan [17]. Comparison of the results with ab initio ones is also given. The effect of choice of reference geometry on the scale factors is also discussed.

COMPUTATIONAL DETAILS

Energy gradients were calculated in both CNDO/2 and MINDO/3 approximations according to Pulay's force method [18, 19] using a modified version of Rinaldi's GEOMO program system [20] with the corrections suggested in ref. 21.

Force constants, i.e., second derivatives of the energy with respect to nuclear coordinates, were calculated numerically by systematic displacements along the internal coordinates shown in Table 1 and Fig. 1. The changes applied were ±2 pm for bond stretchings, ±0.02 rad for in-plane bendings, and 0.1 rad for out-of-plane bendings and ring torsions.

The reference geometries for the harmonic force field calculations were the ones optimized theoretically at their respective levels (the geometries are published in ref. 22), while a complete calculation was carried out with CNDO/2 using the microwave r_s geometry of ref. 23.

To obtain the SQM force fields the theoretical force fields were scaled according to a method described in detail in ref. 1. Off-diagonal force constants of absolute value smaller than 0.05 (in respective units) were omitted. The anharmonic experimental fundamentals of ref. 12 were used during the scaling.

The elements of the M-matrix [24] were used to characterize the normal modes. To compare the semiempirical infrared band intensities with the experimental and ab initio values, the dipole moment derivatives with respect to the internal coordinates were also calculated.

TABLE 1

Internal coordinates for γ-pyrone

No.	Coordinate[a]	Notation[b]	Description
1 . . . 5	$r_1, \ldots, r_5$	$\nu_{C-H}, \nu_{C=O}$	C—H and C=O stretchings
6 . . . 11	$R_1, \ldots, R_6$	$\nu_{C-C}, \nu_{C=C}, \nu_{C-O}$	C—C, C=C and C—O stretchings
12 . . . 16	$\beta_1 = \phi_1 - \phi'_1, \ldots, \beta_5 = \phi_5 - \phi'_5$	$\beta_{C-H}, \beta_{C=O}$	C—H and C=O bendings
17 . . . 19	$\beta' = \alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6$	β'_{ring}	ring deformation
	$\beta'' = 2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6$	β''_{ring}	ring deformation
	$\beta''' = \alpha_2 - \alpha_3 + \alpha_5 - \alpha_6$	β'''_{ring}	ring deformation
20 . . . 24	$\gamma_1, \ldots, \gamma_5$	$\gamma_{C-H}, \gamma_{C=O}$	C—H and C=O out-of-plane bend
25 . . . 27	$t_1 = \tau_1 - \tau_2 + \tau_3 - \tau_4 + \tau_5 - \tau_6$	τ'_{ring}	ring torsion
	$t_2 = 2\tau_1 - \tau_2 - \tau_3 + 2\tau_4 - \tau_5 - \tau_6$	τ''_{ring}	ring torsion
	$t_3 = \tau_2 - \tau_3 + \tau_5 - \tau_6$	τ'''_{ring}	ring torsion

[a] For explanations see Fig. 1. τ_i denotes the torsion around the bond between atoms i and $i + 1$; it is positive when, viewing from the direction of $i + 1$, an anti-clockwise rotation is needed to bring atoms $i + 2$ and $i - 1$ into eclipsed conformation. Normalization factors are omitted. [b] These notations are used in the text.

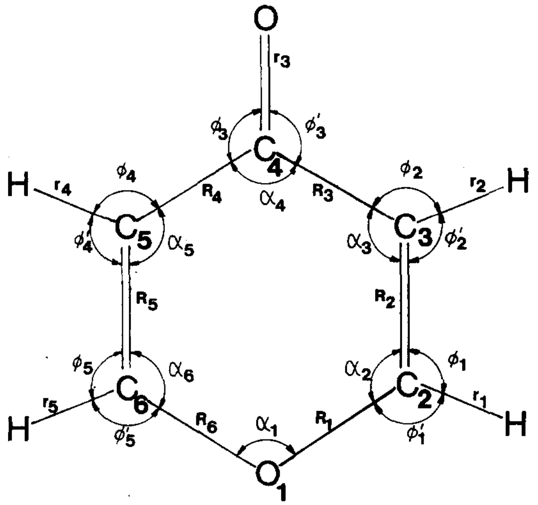

Fig. 1. Representation of in-plane internal coordinates of 4H-pyran-4-one; coordinates used in the calculations are listed in Table 1.

RESULTS AND DISCUSSION

Force fields

For purposes of comparison, the unscaled diagonal force constants obtained by ab initio [12], MINDO/3, and CNDO/2 calculations are shown in Table 2. The SQM CNDO/2 and MINDO/3 force fields of γ-pyrone obtained using the scale factors shown in the second, third and ninth columns of Table 3,

TABLE 2

Unscaled diagonal elements of the force constant matrices obtained by ab initio, MINDO/3 and CNDO/2 methods

Internal coordinates[a]	Diagonal force constants[b]			
	Ab initio	MINDO/3[d]	CNDO/2[d]	
	4-21[c]		I[e]	II[f]
r_1	6.069	6.484	11.659	13.785
r_2	5.988	6.803	11.892	13.647
r_3	12.852	14.886	29.166	33.424
R_1	6.982	8.371	21.537	21.455
R_2	9.510	10.717	22.617	22.171
R_3	5.385	6.426	16.144	14.867
β_1	0.679	0.467	0.732	0.720
β_2	0.567	0.406	0.596	0.604
β_3	1.109	0.704	0.929	0.974
β'	1.647	0.920	1.097	1.148
β''	1.521	0.913	0.919	0.956
β'''	1.542	1.009	1.204	1.233
γ_1	0.591	0.366	0.702	0.696
γ_2	0.560	0.328	0.693	0.689
γ_3	0.807	0.501	0.656	0.691
t_1	0.311	0.151	0.313	0.304
t_2	0.136	0.086	0.061	0.053
t_3	0.422	0.240	0.471	0.474

[a] For notations see Table 1 and Fig. 1. [b] Units are consistent with energy measured in aJ, bond lengths in Å, bond angles in radians. [c] Ref. 12. [d] Present results. [e] Obtained at CNDO/2 optimized reference geometry. [f] Obtained at experimental microwave geometry as reference.

respectively, are available from the authors upon request.

In the case of CNDO/2, as it is expected, the unscaled diagonal stretching force constants are considerably larger than the ab initio values. Some of the bending force constants (e.g., β_{C-H}, γ_{C-H}) are larger, while the others (e.g., $\beta_{C=O}$, $\gamma_{C=O}$, ring deformations) are smaller than the corresponding ab initio values, suggesting the necessity of introducing different scale factors for different type of internal coordinates. As to MINDO/3, the calculated force constants are much closer to the ab initio values, and it can be seen that the stretching constants are overestimated by about 22%, while the bending ones are underestimated by about the same amount.

The coupling force constants obtained by CNDO/2 and MINDO/3 are important only for adjacent bonds, thus showing the non-aromatic character of the compound [23]. Note that the sign of the semiempirical off-diagonal force field elements differ only in a very few cases from the corresponding ab initio values.

Comparing the relative values of the force constants having common scale factors (using a scaling procedure the absolute values have no real importance),

TABLE 3

Empirical scale factors used for corrections of computed CNDO/2 and MINDO/3 force fields

Coordinate[a]	CNDO/2							MINDO/3[g]
	γ-Pyrone[b]		Benzene[c,d] [13]	Pyridine[c,d] [14]	Uracil[e] [15]	MIM[e,f] [16]	Furan[d] [17]	
	I[e]	II[d]						
ν_{C-H}	0.448	0.383	0.382	0.380	0.447	0.445	0.389	0.77
$\nu_{C=O}$	0.355	0.310	—	—	—	0.325	0.365	0.75
ν_{C-O}	0.250	0.260	—	—	—	—	0.243	0.75
$\nu_{C=C}$	0.375	0.385	0.382	0.344	0.404	0.384	0.389	0.83
ν_{C-C}	0.315	0.330	—	—	0.372	0.319	—	0.70
β_{C-H}	0.826	0.780	0.787	0.813	0.623	0.634	0.681	1.15
$\beta_{C=O}$	1.075	0.950	—	—	1.03	1.02	—	1.22
β_{ring}	1.195	1.180	1.19	1.14	1.45	1.42	1.467	1.30
γ_{C-H}	0.650	0.607	—	—	0.535	0.624	0.802	1.21
$\gamma_{C=O}$	0.800	0.810	—	—	1.05	0.759	—	1.20
t_{ring}	0.775	0.775	—	—	0.691	1.150	0.540	1.31

[a] For notations see Table 1 and Fig. 1. [b] Present work. [c] In-plane data have only been published. [d] Experimental geometry was used as reference. [e] CNDO/2 optimized geometry was used as reference. [f] MIM = 1H-pyrrole-2,5-dione. [g] Standard set of ref. 11.

we can conclude that neither CNDO/2 nor MINDO/3 can reproduce the ab initio values exactly. This is the main difference between the semiempirical and the ab initio results, and it follows that none of the methods we used will be as good as the ab initio method in reproducing experimental results [12]. However, as we shall point out later on, the semiempirical results can be good enough to provide a basis for the assignment of an unknown vibrational spectrum.

Regarding the choice of the reference geometry, it should be stated that, because CNDO/2 considerably overestimates the C—H and C=O equilibrium bond lengths, the related diagonal force constants obtained at the CNDO/2 optimized reference geometry are considerably smaller than those determined using the microwave geometry as reference. Other minor differences between the two sets of force field elements can also be seen from the data shown in Table 2. In addition, we note that the signs of the off-diagonal force constants are shown to be independent of the choice of reference geometries.

Scale factors

The values of the scale factors used to correct the directly computed CNDO/2 and MINDO/3 force fields to obtain the corresponding SQM force fields are shown in Table 3. The optimized CNDO/2 scale factors are not very different from those obtained for other molecules. (See columns 4—8 of Table 3.)

The CNDO/2 scale factors of γ-pyrone for ν_{C-H} and $\nu_{C=O}$ are somewhat different depending upon the choice of the reference geometry. This is mainly related to the overestimated bond lengths at CNDO/2 level but is also partly due to the anharmonicity. This feature can be observed for ν_{C-H} scale factors of other molecules shown in Table 3: in the case of uracil [15] and maleimide [16], the optimized geometries were chosen as reference, while for the other three compounds experimental reference geometries were used.

According to our present results and those listed in ref. 11, small variations in the reference geometry have no drastic influence on the optimized values of the scale factors. The frequency is approximately proportional to the square root of the related diagonal force constant, so a relatively large 10% change in the scale factor (i.e., in the force constant) will cause a variation in the vibrational frequency of less than 5%. This means that small changes in the reference geometry do not affect the assignment of the spectrum. Thus, within the expected error limit of the semiempirical calculations, if a well established set of scale factors is readily available, the reference geometries used in evaluation of the force constants may be taken from any reliable source without influencing the assignments based on the theoretical calculations.

Some of the scale factors for the same internal coordinate are different from molecule to molecule because misassigned vibrational fundamentals were used during the optimization of the scale factors (e.g., see refs. 9 and 10 for maleimide and uracil respectively). Thus, it should be emphasized that one must be very careful using any type of scaling, because without a well established initial set of scale factors, taken from similar molecules, the optimization of the scale factors may lead to incorrect results. To show how reliable a "standard" scale factor set can be we cite the present results at MINDO/3 level.

Vibrational frequencies

The calculated and the measured fundamental vibrational frequencies of γ-pyrone are shown in Table 4. It is seen that both the SQM CNDO/2 and MINDO/3 force fields reproduce well the in-plane frequencies. The calculated $\gamma_{C=O}$ and γ_{C-H} frequencies are quite acceptable as well. However, the semiempirical force fields do not reproduce the ring bendings and ring torsions well. For example in the case of CNDO/2, the largest deviations between the experimental and calculated frequencies are found for these vibrations, 42 cm^{-1} for ring bending ν_{21} and 54 cm^{-1} for ring torsion ν_{26}. The reason for this is that the frequencies of the a_1 symmetry ring bendings and the b_2 symmetry ring torsions are underestimated, while those of the b_1 symmetry ring bendings and the a_2 symmetry ring torsions are overestimated. Scaling the bendings and torsions separately according to their symmetry improved the results for the ring bendings, but left essentially intact the results for ring torsions. We do not think, however, that the introduction of more and more scale factors provides a practical way for detailed interpretation of the

TABLE 4

Experimental and calculated vibrational fundamentals for γ-pyrone[a]

ν_i	Symmetry	Description[b]	Exp. [12]	Calculated			
				CNDO/2[e]		MINDO/3[c]	Ab initio[d]
				I[e]	II[f]		
1	a_1	ν_{C-H}	3098	3106	3095	3078	3101
2	a_1	ν_{C-H}	3076	3070	3075	3002	3067
3	a_1	$\nu_{C=O} + \nu_{C=C}$	1702	1715	1716	1687	1715
4	a_1	$\nu_{C=O} + \nu_{C=C}$	1652	1650	1641	1639	1642
5	a_1	β_{C-H}	1385	1400	1399	1362	1382
6	a_1	β_{C-H}	1193	1186	1190	1179	1201
7	a_1	$\beta_{ring} + \beta_{C-H}$	1010	997	1006	1012	1011
8	a_1	$\beta_{C-H} + \beta_{ring}$	920	900	904	896	908
9	a_1	ν_{C-C}	825	794	787	790	803
10	a_1	β_{ring}	502	463	468	490	494
11	a_2	γ_{C-H}	960	967	948	904	976
12	a_2	γ_{C-H}	790	800	794	835	793
13	a_2	τ_{ring}	395	423	420	414	398
14	b_1	ν_{C-H}	3098	3111	3096	3078	3098
15	b_1	ν_{C-H}	3076	3073	3077	3001	3067
16	b_1	$\nu_{C=C}$	1610	1597	1597	1566	1590
17	b_1	$\nu_{C-C} + \beta_{C-H}$	1401	1440	1436	1346	1405
18	b_1	$\beta_{C-H} + \nu_{C-O}$	1314	1285	1281	1234	1322
19	b_1	$\beta_{C-H} + \beta_{C=O}$	1216	1245	1244	1147	1217
20	b_1	$\nu_{C-O} + \beta_{C-H}$	1019	1030	1059	1041	1020
21	b_1	$\beta_{ring} + \nu_{C-O}$	625	667	662	636	637
22	b_1	$\beta_{C=O} + \beta_{ring}$	458	456	460	462	434
23	b_2	γ_{C-H}	960	962	943	920	970
24	b_2	$\gamma_{C=O} + \gamma_{C-H}$	847	852	859	847	848
25	b_2	$\tau_{ring} + \gamma_{C=O}$	720	738	740	724	714
26	b_2	$\tau_{ring} + \gamma_{C=O}$	424	370	377	433	429
27	b_2	τ_{ring}	149	99	97	159	155
χ (in-plane)				20.5	20.5	25.4	6.6
χ (out-of-plane)				33.4	34.3	17.0	3.9

[a] Frequencies (ν) and weighted mean deviations (χ) are in cm^{-1}. [b] Based on M-matrix method [24]; for notations see Table 1 and Fig. 1. [c] Present results. [d] 4-21 basis set; calculation III of ref. 12, refined scale factors. [e] Obtained at CNDO/2 optimized reference geometry. [f] Obtained at microwave geometry as reference.

vibrational spectra. This procedure might be justified only if one wants to investigate very similar molecules with a great accuracy; however, in those cases it seems preferable to turn to calculations of higher precision.

Finally, note that the semiempirical dipole moments derivatives cannot be used even for a semiquantitative description of the infrared band intensities, as it was also shown in previous studies [11, 13—17].

CONCLUSIONS

The scaling procedure of ref. 1 has been applied to correct the directly computed CNDO/2 and MINDO/3 force fields of γ-pyrone. The vibrational frequencies calculated from these SQM force fields agree reasonably well with the experimental and ab initio results [12], except for the τ_{ring} out-of plane ring torsion modes in the case of CNDO/2 and for the $\gamma_{\text{C—H}}$ out-of-plane bendings in the case of MINDO/3.

The optimized CNDO/2 scale factors for γ-pyrone are not very different from those optimized for other molecules. The results using the recommended standard scale factors of ref. 11 for corrections of the computed MINDO/3 force field also confirm transferability of scale factors between molecules with similar structures. This assures the applicability of semiempirical methods in vibrational studies on medium and large molecules, where the basic problem of the assignment of the fundamentals is usually unresolvable by the traditional techniques based on normal coordinate analysis. Based on the results presented in this work, we advise use of a standard set of scale factors to correct the theoretical force field. An optimization of the scale factors can be a logical next step, but the assignment must be based on the first set of frequencies and normal modes. We note, additionally, that the overall power of MINDO/3 does not exceed that of CNDO/2: the applicability of these methods for vibrational force field calculations seems to be the same.

Studying the effect of the choice of reference geometry on the scale factors, we conclude that the application of different (optimized or experimental) reference geometries (if they do not differ significantly, which usually holds) does not cause drastic differences in the scale factors. Our results are supported by Shaw et al. [25], who within an ab initio study demonstrated that optimized values of scale factors are strongly dependent on the basis set, but are almost independent of the quality of geometries used in force field calculations and scale factor optimization. However, for systematic studies of molecular families, it is desirable to use reference geometries obtained in the same way; though even in this case it is hard to avoid the difficulties arising from the fact that semiempirical calculations sometimes underestimate and sometimes overestimate the length of a certain bond even in similar molecules.

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