QUANTUM CHEMICAL PREDICTION OF 2*H*-PYRAN VIBRATION SPECTRUM

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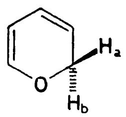
Dedicated to Professor Otto Exner on the occasion of his 65th birthday.

Ab initio MO optimization of the 2*H*-pyran molecule leads to a defined equilibrium geometry of this so far not identified heterocyclic molecule and to a physical justification of its existence. More advanced nonempirical wavefunctions and temperature corrections indicate that heterocyclic molecule *I* is energetically less stable than non-cyclic isomers *II* and *III*. Wavenumbers of fundamental vibrational transitions of heterocycle *I* and also known (2*E*)-2,4-pentadienal (*IIIb*) were calculated using 3-21G wavefunctions. The vibrational spectrum of compound *I* is predicted on the basis of correlation corrections.

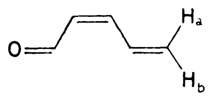
Unsubstituted 2*H*-pyran molecule *I* despite the permanent synthetic effort[1–4] still escapes attempts at identification. Successful semiempirical MO-optimizations[5–7] of this heterocyclic molecule can be considered as an argument in favour of the physical justification of its existence. It can correspond to a local minimum on the C_5H_6O system energy hypersurface along with the other energy minima for (2*Z*)- and (2*E*)-2,4-pentadienal conformers *II* and *III*.

The cause of unstability of molecule *I* is most probably connected with valence tautomerism $I \rightleftarrows II$ and the related thermal isomerization $II \rightarrow III$ proved experimentally. So far it can be hardly concluded more explicitly whether the reason for cyclic form *I* not to have been identified as yet lies in the extreme shift of the $I \rightleftarrows II$ equilibrium to the right as a consequence of the high energetic stability of molecule *II* or in the drain of (2*Z*)-isomer *II* due to its irreversible isomerization to the (2*E*)--isomer *III*. So far the MO calculations of semiempirical and non-empirical SCF energies of molecules *I*–*III* lead to controversial results preferring either the cyclic[5–7] or non-cyclic[5] forms. Some uncertainty in the comparison of these studies is due to the difference between methods used for the molecular geometry optimization and calculations of energetic or other observable physical quantities.

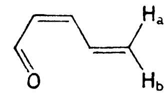
Therefore, we have decided in the present work to carry out the MO calculation of optimized molecular geometry of heterocyclic molecule *I* with an identical non-empirical basis set of AO (3-21G) and to predict its theoretical vibrational spectra which can be usable in future for experimental attempts at the identification of molecule *I* generated under various physical conditions. Besides, we have compared some energetic data obtained for molecules *I*–*III* using alternative basis sets of AO.



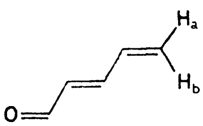
I



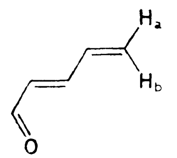
IIa



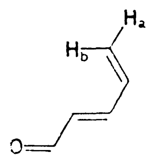
IIb



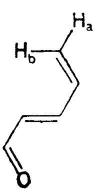
IIIa



IIIb



IIIc



IIId

CALCULATIONS

The Gaussian 80 program with the standard basis sets STO-3G, 3-21G and 6-31G* was used throughout the entire study. The input approximations of molecular structures *II* and *III* were based on results of the CNDO/2 model[5] the terminal fragments being asymmetrically twisted by 5° from the plane of the central double bond.

The energy values of the 3-21G optimized models of the studied compounds are summarized in Table I.

RESULTS AND DISCUSSION

The effort to minimize the energy of all the studied molecular geometries by a non--empirical approach of the STO-3G as well as the 3-21G basis sets was positive. In agreement with the previously carried out semiempirical optimization procedures[5–7] it is possible to conclude that all the further discussed molecular forms have certain energetic minima on the 5 C + 6 H + O system energy hypersurface. This means that the existence of these molecular systems is physically justified.

Molecular Structures

The calculated internal coordinates of molecules *I–III* are summarized in Tables II and III. As the present optimization method leads to a very good agreement with experimental structural data[8] for different organic compounds we presume that the calculated values represent the so far best approximation of the real and up to now uknown molecular geometries of compounds *I–III*. The non-empirically calculated internal coordinates of 2*H*-pyran molecule *I* (see Table II) only in some minor details differ from the values determined using semiempirical methods[5]. Heterocycle *I* seems to be only slightly distorted from planarity of twisted envelope. From the viewpoint of calculated bond lengths C—C, C=C, and C—O the 3-21G model of compound *I* shows higher degree of electron localization. The valence angles, with the probably only exception of the O(1)—C(2)—C(3) angle, are very similar to those of the CNDO/2 model[5]. Considerable differences arise, however, in the torsional angles which are probably the most sensitive to the choice of method and the basis set used for their optimization. Similarly striking are these differences in both non-empirical basis sets – STO-3G and 3-21G (see Table I). The first predicts an almost planar heterocyclic ring like the CNDO/2 model[5].

TABLE I

STO-3G and 3-21G energies of molecules *I–III* at their optimized geometries[a]

Compound	Method STO-3G	3-21G
I[b]	−264·302416	−266·156001
IIa	−264·247429	−266·145405
IIb	−264·248091	−266·150004
IIIa	−264·251121	−266·150280
IIIb[b]	−264·250627	−266·151295
IIIc	−264·248283	−266·145110
IIId	−264·247724	−266·145942

[a] All numerical values are given in dimensionless units defined as $E = E_{tot}/h$, where $h =$ $= 2\,628{\cdot}1$ kJ mol^{-1}; [b] corresponding 6-31G*//3-21G total energies are: (*I*) −267·640592, (*IIIb*) −267·648928.

TABLE II

Optimized STO-3G and 3-21G geometries of molecule *I*

Atoms	Bond length, pm		Atoms	Bond angles, deg		Atoms	Dihedral angles, deg	
	STO-3G	3-21G		STO-3G	3-21G		STO-3G	3-21G
O(1)–C(2)	144·8	145·6	O(1)–C(2)–C(3)	116·8	112·6	C(4)–C(3)–C(2)–O(1)	−1·9	20·2
C(2)–C(3)	152·9	151·4	C(2)–C(3)–C(4)	121·7	120·6	C(5)–C(4)–C(3)–C(2)	0·2	−2·9
C(3)–C(4)	131·2	132·0	C(3)–C(4)–C(5)	119·1	120·3	C(6)–C(5)–C(4)–C(3)	0·8	−9·3
C(4)–C(5)	147·9	146·9	C(4)–C(5)–C(6)	119·2	118·7	H(6)–C(6)–C(5)–C(4)	179·6	−175·6
C(5)–C(6)	131·9	132·0	C(5)–C(6)–O(1)	126·8	123·5	H(5)–C(5)–C(4)–C(3)	−179·5	173·6
C(6)–C(1)	138·9	137·4	C(6)–O(1)–C(2)	116·5	118·9	H(4)–C(4)–C(3)–C(2)	−179·9	178·9
H(6)–C(6)	108·9	106·9	H(6)–C(6)–C(5)	122·8	124·7	H(3)–C(3)–C(2)–O(1)	179·4	160·9
H(5)–C(5)	107·9	106·9	H(5)–C(5)–C(4)	120·1	120·6	H(a)–C(2)–C(3)–C(4)	120·3	141·2
H(4)–C(4)	108·3	107·2	H(4)–C(4)–C(3)	122·0	121·1	H(b)–C(2)–C(3)–C(4)	−123·6	−98·2
H(3)–C(3)	108·2	107·2	H(3)–C(3)–C(2)	115·3	117·0	C(3)–C(2)–O(1)–C(6)	2·5	17·1
H(a)–C(2)	109·9	108·6	H(a)–C(2)–O(1)	107·4	108·1	C(2)–O(1)–C(6)–C(5)	−1·7	2·1
H(b)–C(2)	109·9	108·0	H(b)–C(2)–O(1)	107·0	105·6	O(1)–C(6)–C(5)–C(4)	0·0	−26·9

The molecular geometry of the non-cyclic isomers *II* and *III* (Table III) corresponds to a completely planar configuration of all atomic centers and thus is strikingly different from the analogous non-planar molecular forms calculated[6,7] by the MINDO/3 and MNDO methods. This difference is undoubtedly the consequence of the unreliability of the NDO-type methods for the calculation of conformational geometry of the π-electron systems[9–11]. Table III further shows that non-empirically calculated bond lengths and angles for characteristic pairs resp. triplets of atomic

TABLE III
Optimized 3-21G geometries of molecules *II* and *III*

Parameter	Compound					
	IIa	*IIb*	*IIIa*	*IIIb*	*IIIc*	*IIId*
Bond lengths, pm						
O(1)–C(2)	121·3	121·6	121·1	121·4	121·1	121·4
C(2)–C(3)	146·8	146·8	146·7	147·0	146·7	147·1
C(3)–C(4)	132·7	133·0	132·4	132·6	132·4	132·5
C(4)–C(5)	146·6	146·4	146·1	145·9	147·1	147·0
C(5)–C(6)	132·2	132·2	132·1	132·2	132·1	132·1
H(2)–C(2)	108·3	108·6	108·8	108·5	108·8	108·5
H(3)–C(3)	107·2	107·3	107·3	107·3	107·2	107·2
H(4)–C(4)	107·5	107·6	107·8	107·5	107·7	107·5
H(5)–C(5)	107·2	106·8	107·4	108·5	107·4	107·4
H(a)–C(6)	107·5	107·2	107·2	107·2	107·2	107·2
H(b)–C(6)	107·1	107·5	107·4	107·4	107·3	107·3
Bond angles[a], deg						
O(1)–C(2)–C(3)	123·0	126·8	124·5	124·3	124·4	124·4
C(2)–C(3)–C(4)	125·6	125·8	121·0	120·3	120·5	119·9
C(3)–C(4)–C(5)	127·5	126·6	124·6	124·9	127·2	127·4
C(4)–C(5)–C(6)	122·1	121·7	122·3	123·0	126·0	126·1
H(a)–C(6)–C(5)	121·4	121·5	121·7	121·8	121·1	121·2
H(b)–C(6)–C(5)	122·1	122·1	121·9	121·8	122·7	122·7
H(5)–C(5)–C(6)	119·4	121·8	120·2	120·2	118·9	119·0
H(4)–C(4)–C(5)	114·5	115·4	116·1	117·2	114·7	115·9
H(3)–C(3)–C(4)	120·0	119·4	122·1	122·1	123·0	122·9
H(2)–C(2)–C(3)	116·5	113·2	114·3	114·8	114·4	114·7
H(a)–C(6)–H(b)	116·5	116·3	116·4	116·5	116·2	116·1

[a] All the atoms lie in the same plane.

centers differ only slightly. The difference between both non-empirical basis sets is also very small.

Molecular Geometries

According to results of the MNDO study[7] it can be concluded that the electrocyclic ring opening of molecule *I* may proceed either by formation of 2*Z*-isomer *II* (path A) or directly to the formation of 2*E*-isomer *III* (path B). Path B seems to be even energetically preferred, according to the calculated energy barriers. The values of these barriers ($\sim$84 kJ mol^{-1} and lower) though suggest that at common temperatures both paths A and B can be considered as valence tautomerism and described as either two formally independent equilibria $I \rightleftarrows II$ and $I \rightleftarrows III$ or rather as a single equilibrium system $I \rightleftarrows II \rightleftarrows III$ or $II \rightleftarrows I \rightleftarrows III$, respectively. From experimental information it may be concluded that the thermodynamically most stable form is 2*E*-isomer *III*.

The differences in non-empirically calculated molecular energies ΔE of the energetically most favourable cyclic form *IIIb* and the heterocycle *I* are presented in Table IV. It is obvious that the relative energetic stability of molecules *I* and *IIIb* thus dramatically depends on the used AO basis set. Minimal basis set STO-3G unrealistically prefers the 2*H*-pyran (*I*) structure by 136 kJ mol^{-1} like the semi-empirical methods[5-7]. During the transition to the 3-21G basis set this energetic preference is decreased by one order of magnitude. It is, therefore, evident (see Table IV) that by a gradual increase of wavefunction quality in the *ab initio* MO method the apparent energetic preference of heterocyclic form *I* gradually vanishes. While using the 6-31G* basis set and after corrections to room temperature the ΔE values become negative and the theoretical prediction then thermodynamically prefers the non-cyclic (2*E*) form *IIIb* in accordance with the already existing experimental difficulties to identify heterocyclic tautomer *I*. The observed trend also agrees with the experimental experience gathered in the quantum chemical literature, i.e., that comparing of structures with different numbers of π-bonds requires the use of

TABLE IV

Comparison of calculated molecular energy differencies $\Delta E = E(III) - E(I)$ for compounds *I* and *IIIb* (in kJ mol^{-1})

Method	STO-3G	3-21G	3-21G[a]	6-31G	6-31G*[a]
ΔE	+136·1	+12·4	+7·6	−21·9	−29·8

[a] Corrected for 298 K.

more flexible basis sets. This is because calculations with small basis sets ascribe to saturated compounds an exaggerated stability relative to the corresponding unsaturated compounds[17,18].

In connection with the above described interpretation the question concerning the possible role of the alternative open (2Z)-form *IIb* arises. It was shown in the previous paper[5] that for the CNDO/2 optimized geometries of the *I* and *IIb* isomers the STO-3G molecular energies show a seeming preference of cyclic form *I* by 141·9 kJ mol^{-1}, but the application of the 4-31G again leads to a change of situation so that the non-cyclic isomer *IIb* becomes slightly more preferred (−3·7 kJ mol^{-1}). In the present calculation of the STO-3G molecular energies for STO-3G optimized molecule models of *I* and *IIb* we have found the appaerent energetic preference of heterocycle *I* to be 142·8 kJ mol^{-1}, i.e. almost exactly the same as for the CNDO/2 optimized models. We can therefore conclude that both the CNDO/2 and 3-21G molecular geometries lead to insignificant differences in calculated molecular energies by given method and that the interpretation of the 4-31G energies is, therefore, physically justified. Similarly as in the case of comparison of the *I* and *IIIb* molecules (Table IV) we can also expect the annuling of the apparent energetic preference of the heterocyclic form *I* during transfer to calculation using more perfect basis sets of AO. In accord with these findings the difference in 3-21G energies of the molecules *I* and *IIb* is only 15·8 kJ mol^{-1}. The use of the 4-31G and 6-31G* basis set including temperature corrections would undoubtedly lead to negative values of the ΔE energy difference and thus to preference of the non-cyclic isomer *IIb*.

The equilibrium among the molecules *I*, *II*, and *III* can be, however, accompanied by conformation and isomerization interconversions of both isomeric 2,4-pentadienals.

TABLE V

Calculated enthalpies of interconversions between configurational forms *II* and *III* of 2,4-pentadienal

Configurational change	Equilibrium (2*Z*) ⇄ (2*E*)	ΔH^0_0, kJ mol^{-1} STO-3G	ΔH^0_0, kJ mol^{-1} 3-21G
C—C=C—C isomerization	*IIb* ⇄ *IIIb*	−6·7	−3·4
	IIa ⇄ *IIIa*	−9·7	−12·8
C=C—C=C conformation	*IIIb* ⇄ *IIId*	+7·6	+14·0
	IIIa ⇄ *IIIc*	+7·5	+13·6
C=C—C=O conformation	*IIb* ⇄ *IIa*	+1·7	+12·0
	IIIb ⇄ *IIIa*	−1·3	+2·6
	IIId ⇄ *IIIc*	−1·4	+2·2

The quantum chemical interpretation of some of the physical properties of these compounds[12-14] have shown the necessity of further conformers *IIa*, *IIIa*, and *IIIc*–*d* to be taken into account. Table V presents the calculated energy changes connected with individual equilibrium processes of the corresponding 3-21G optimized models *II* and *III*. It is obvious that, with the exception of the *IIb* ⇄ *IIIb* equilibrium, the use of 3-21G molecular energies leads to somewhat more marked energy effects which are almost comparable with the energies of electrocyclization *I* ⇄ *II* or *I* ⇄ *III*. With the exception of the exoergic isomerization *IIa* → *IIIa* which is probably responsible for the easy thermic conversion of the (2*Z*)-2,4-pentadienal to the corresponding (2*E*)-isomer[3], the remaining processes are more or less endoergic. We cannot exclude from further consideration that the processes presented in Table V may in real conditions entropically facilitate the electrocyclic decomposition of the heterocycle *I*.

Vibrational Spectra

With respect to a perspective possibility of the identification of not yet known 2*H*-pyran molecules we have made here an attempt at calculation of the corresponding vibrational spectrum from the optimized 3-21G geometries and energies. To this purpose, we have first calculated wavenumbers of all fundamental vibrational transitions of (2*E*)-2,4-pentadienal, represented by the *IIIb* conformer, and then selected those which can be assigned to band maxima in the known infrared absorption spectrum[15]. Figure 1 shows that there is a strong linear correlation between the calculated and experimental excitation energies which are represented by the transi-

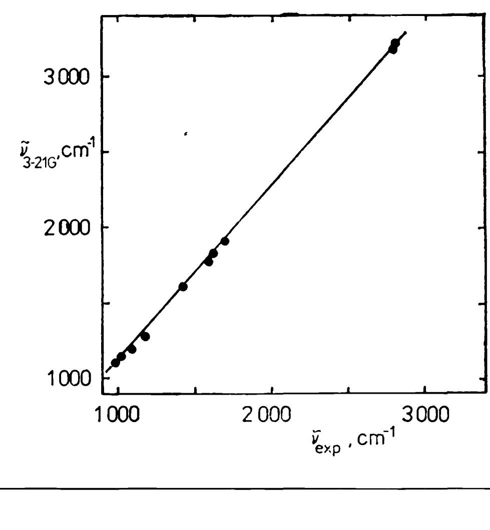


FIG. 1
Theoretical vs experimental[15] vibronic modes of (2*E*)-2,4-pentadienal (*IIIb*)

tion wavenumbers. The correlation can be expressed by a linear regression

$$\tilde{\nu}_{3-21G} = a\tilde{\nu}_{exp} + b \qquad (A)$$

with the following characteristics: $a = 1{\cdot}1776$, $b = -60{\cdot}85$, $r = 0{\cdot}999$ for ten points.

TABLE VI

Theoretical vibronic modes of molecules *I* and *IIIb* (in cm^{-1})

(2*E*)-2,4-Pentadienal (*IIIb*)			2*H*-Pyran (*I*)	
$\tilde{\nu}_{exp}$	$\tilde{\nu}_{3-21G}$	$\tilde{\nu}_{calc}$ [a]	$\tilde{\nu}_{3-21G}$	$\tilde{\nu}_{calc}$
	143	176	99	139
	167	196	360	360
	213	236	554	525
	317	323	615	576
	373	371	680	632
	528	502	817	748
601	719	664	896	814
634	802	734	914	830
	1 008	909	981	886
	1 032	929	1 006	908
	1 082	972	1 073	965
	1 119	1 003	1 137	1 119
996	1 164	1 041	1 156	1 035
1 017	1 179	1 054	1 175	1 051
1 108	1 199	1 063	1 197	1 070
1 170	1 292	1 150	1 328	1 181
	1 433	1 269	1 373	1 219
	1 460	1 292	1 389	1 233
	1 482	1 311	1 505	1 330
	1 569	1 384	1 540	1 360
1 421	1 614	1 423	1 581	1 395
1 593, 1 589	1 799	1 579	1 683	1 481
1 637	1 845	1 619	1 799	1 580
1 684	1 909	1 673	1 862	1 633
2 796	3 190	2 758	3 182	2 751
2 820	3 321	2 869	3 271	2 827
	3 334	2 880	3 355	2 898
	3 345	2 889	3 379	2 918
	3 365	2 906	3 398	2 934
	3 405	2 940	3 425	2 957

[a] Empirically corrected 3-21G frequencies (see text).

On the assumption of general validity of regression (A) for the compounds under study the theoretical estimations of wavenumbers $\tilde{\nu}_{calc}$ for the *IIIb* molecule were calculated using

$$\tilde{\nu}_{calc} = a^{-1}(\tilde{\nu}_{3-21G} - b) \qquad (B)$$

From Table VI a satisfactory agreement of the $\tilde{\nu}_{exp}$ and $\tilde{\nu}_{calc}$ values is obvious. Using the same dependence in the case of $\tilde{\nu}_{3-21G}$ values calculated for the heterocycle *I* we have obtained the $\tilde{\nu}_{calc}$ values which can be considered to be theoretically justified predictions of all fundamental vibrational modes of the yet unidentified (2*H*)-pyran, part of which can be observed in its vibration-rotation spectrum. From the analogy with the known[16] $\tilde{\nu}_{max}$ values of characteristic vibrations ν_1(C=C) and ν_2(C—O—C) of simpler 2*H*-pyrans, i.e. 2,3,4,6-tetramethyl-2*H*-pyran ($\nu_1 = 1\,632,\ 1\,680,\ \nu_2 = 1\,122$) or 2,2,3,6,-tetramethyl-5-phenyl-2*H*-pyran ($\nu_1 = 1\,610,\ 1\,660,\ \nu_2 = 1\,150$ to $1\,200$) it is clear that the characteristic maxima of vibrational bands in the spectrum of compound *I* will probably be $\nu_1 = 1\,580,\ 1\,633,\ \nu_2 \doteq 1\,070-1\,180\ \text{cm}^{-1}$. Comparison of the compounds *I* and *IIIb* shows that their spectra markedly differ especially in the lower wavenumber region where compound *I* has a characteristic absorption between 800 and 900 cm^{-1} while compound *IIIb* has obviously no absorption.

It is evident that extrapolation of the correlation (B) to wavenumbers below 600 cm^{-1} is problematic. This region, however, seems to be of lower spectroscopical interest.

CONCLUSION

The unsubstituted 2*H*-pyran *I* is according to a more detailed non-empirical MO-SCF calculation a thermodynamically unstable compound with a short lifetime at common temperatures which makes its identification under such conditions very little promising. On the contrary, its physical justification by the existence of a corresponding minimum on the energy hypersurface gives a good chance to identify this molecule at lower temperatures by means of suitable cryogenic and spectroscopic techniques.

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