

# MO STUDY OF MOLECULAR AND ELECTRONIC STRUCTURE OF 2,2-DIMETHYL-2H-PYRAN AND ITS ACYCLIC VALENCE ISOMERS

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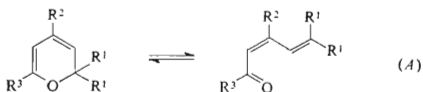
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CNDO/2, MNDO, STO-3G, and 4-31G MO calculations of *I* to *IIId* molecules have been carried out. The effect of the presence of two methyl groups in the studied systems on their molecular and electronic structure and on valence isomerism (*A*) is discussed.

On the basis of the experimental facts known until now<sup>1-8</sup>, it is obvious that the valence isomerism of 2*H*-pyran derivatives represented by the electrocyclic process (*A*) is strongly affected by the circumstance whether or not the substituents  $R^1$  to  $R^3$  are alkyl groups. In the case of the parent substances, *i.e.*  $R^1 = R^2 = R^3 = H$  the equilibrium (*A*) is obviously shifted to the right<sup>1-3</sup> in accordance with the relative values of molecular energies calculated<sup>9</sup> for zero point by means of the *ab initio* MO method using the 4-31G basis. On the contrary, the cases in which  $R^1$  and  $R^2 \neq H$  lead to the equilibria (*A*) shifted to the left, and the cyclic valence isomers can be isolated<sup>10</sup>. With the aim to contribute to elucidation of the logical presumption that the condition  $R^1 \neq H$  could be a decisive factor for the preference of the heterocyclic valence isomers in the process (*A*), we decided to study in detail the equilibrium (*A*) for



the elementary case  $R^1 = CH_3$  and  $R^2 = R^3 = H$  using semiempirical and non-empirical MO approaches. The following results are based on systematic CNDO/2, STO-3G, and 4-31G calculations of the molecules of 2,2-dimethyl-2*H*-pyran (*I*), two conformers of (*Z*)-5-methyl-2,4-hexadienal (*IIa, b*), and four conformers of the corresponding (*E*)-isomer *IIIa-IIIId*, and some additional MNDO calculations.

## CALCULATIONS

All the non-empiric calculations were carried out with the use of Gaussian 76 program adapted for calculation of extensive molecular structures. The semiempirical optimizations of molecular

geometries were carried out with standard programs. The MNDO gradient optimization<sup>12-14</sup> was used to verify whether or not the CNDO/2 gradient optimization<sup>11</sup> of the models *I* and *Ib* ( $R = CH_3$ ) with various numbers of  $\pi$  electrons gives their molecular geometries with different relative accuracy. The calculation of 4-31G total energies only used the two-electron integrals in absolute value greater than  $1 \cdot 10^{-5}$ . For the structure *I*,  $R = CH_3$ , effect of this approximation on accuracy of the calculated total energy was investigated, and the two calculated values were found to differ by  $0.22 \text{ kJ mol}^{-1}$  only. As the differences in total energies of the studied structures are greater by one order of magnitude, the approximatively calculated values can be considered sufficient for our study.

To enable complete comparison of relative energies of all conformers of the acyclic valence isomers *Ia-IIIId* ( $R = CH_3$ ) with analogous unsubstituted conformers of 2,4-pentadienal, the results of ref.<sup>9</sup> were now extended by full CNDO/2 gradient optimization of the non-substituted structures *Ib*, *IIIb-IIIId* ( $R = H$ ) and their non-empirical calculations. The calculated molecular geometries of the unsubstituted structures are given in Table I. In connection with the CNDO/2 gradient optimization of the substituted dienal structures it is worth mentioning that this procedure failed in the case of structure *Ia* ( $R = CH_3$ ) where the obtained structure (according to its geometry parameters) cannot represent a stable chemical substance.

## RESULTS AND DISCUSSION

### Molecular Structure

Table II gives results of the CNDO/2 gradient optimization of structures *Ia*, *IIIa* to *IIIId*. The calculated geometries of all the open forms *Ia-IIIId* ( $R = CH_3$ ) show

TABLE I

Structural parameters of the unsubstituted models *Ib*, *IIIb-IIIId* obtained by the CNDO/2 gradient optimization. All the structures are fully planar, the bond lengths in pm, the bond angles in  $^\circ$

Bond	<i>Ib</i>	<i>IIIb</i>	<i>IIIc</i>	<i>IIIId</i>	Bond angle	<i>Ib</i>	<i>IIIb</i>	<i>IIIc</i>	<i>IIIId</i>
O—C(1)	126.5	126.4	126.4	126.4	O—C(1)—C(2)	126.1	125.9	125.7	125.9
C(1)—C(2)	142.9	143.0	143.1	143.0	C(1)—C(2)—C(3)	126.2	125.5	125.6	125.5
C(2)—C(3)	133.0	134.0	133.9	134.0	C(2)—C(3)—C(4)	128.3	128.1	129.5	129.3
C(3)—C(4)	143.6	143.6	143.6	143.6	C(3)—C(4)—C(5)	126.2	126.6	128.4	128.2
C(4)—C(5)	132.5	132.5	132.5	132.5	H(1)—C(1)—O	116.0	116.0	116.2	116.0
H(1)—C(1)	112.3	112.3	112.3	112.3	H(2)—C(2)—C(1)	114.8	115.0	115.1	115.1
H(2)—C(2)	111.8	111.8	111.9	111.8	H(3)—C(3)—C(2)	117.4	117.5	117.0	116.9
H(3)—C(3)	112.1	112.1	112.1	112.1	H(4)—C(4)—C(3)	115.2	115.4	114.6	114.6
H(4)—C(4)	112.0	112.0	112.0	112.0	H(a)—C(5)—C(4)	124.1	124.1	124.0	124.1
H(a)—C(5)	111.3	111.3	111.2	111.2	H(b)—C(5)—C(4)	124.5	124.4	124.5	124.5
H(b)—C(5)	111.3	111.3	111.3	111.3	H(a)—C(5)—H(b)	111.3	111.4	111.5	111.5

TABLE II

Comparison of the structural parameters of *Ila*, *IIIa–IIIc* models ( $R = CH_3$ ) obtained by CNDO/2 gradient optimization

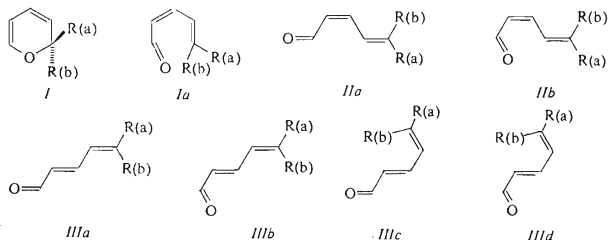
Compound	<i>Ila</i>	<i>IIIa</i>	<i>IIIb</i>	<i>IIIc</i>	<i>IIIc</i>
Bond lengths, pm					
O—C(1)	126.5	126.5	126.6	126.5	126.5
C(1)—C(2)	142.9	142.9	142.7	142.8	142.7
C(2)—C(3)	134.2	134.3	134.4	134.4	134.5
C(3)—C(4)	143.1	143.0	143.0	142.7	142.7
C(4)—C(5)	135.0	135.1	135.1	135.4	135.4
C(a)—C(5)	145.6	145.5	145.5	145.5	145.5
C(b)—C(5)	145.7	145.8	145.8	145.8	145.7
H(1)—C(1)	112.4	112.4	112.4	112.4	112.4
H(2)—C(2)	111.9	111.8	111.8	111.9	111.8
H(3)—C(3)	112.2	112.2	112.2	112.2	112.2
H(4)—C(4)	112.1	112.1	112.1	112.1	112.1
H—C(a)	112.0	112.0	112.0	112.2	112.2
H'—C(a)	112.1	112.1	112.1	112.1	112.1
H''—C(a)	112.1	112.1	112.1	112.1	112.1
H—C(b)	112.1	112.0	112.1	112.1	112.1
H'—C(b)	112.0	112.0	112.0	112.0	112.0
H''—C(b)	112.1	112.0	112.1	112.1	112.1
Bond angles (°)					
O—C(1)—C(2)	125.9	126.3	126.1	126.0	126.3
C(1)—C(2)—C(3)	126.7	125.0	125.0	125.5	125.0
C(2)—C(3)—C(4)	129.0	128.8	128.7	130.5	130.8
C(3)—C(4)—C(5)	129.1	128.6	128.6	129.3	129.3
C(a)—C(5)—C(4)	124.7	124.2	124.3	122.7	122.5
C(b)—C(5)—C(4)	121.6	122.0	121.8	120.7	120.8
H(1)—C(1)—O	115.9	116.0	115.8	116.0	115.9
H(2)—C(2)—C(1)	114.7	115.4	115.5	114.8	115.1
H(3)—C(3)—C(2)	116.6	116.7	116.6	116.3	115.9
H(4)—C(4)—C(3)	113.7	113.9	113.9	113.5	113.5
H—C(a)—C(5)	114.9	115.1	115.2	111.9	111.9
H'—C(a)—C(5)	111.2	111.0	110.9	113.9	114.0
H''—C(a)—C(5)	111.2	111.0	110.9	111.9	111.9
H—C(b)—C(5)	114.4	111.9	111.8	111.8	111.8
H'—C(b)—C(5)	111.4	114.1	114.2	114.5	114.5
H''—C(b)—C(5)	111.4	111.9	111.8	111.8	111.8
C(a)—C(5)—C(b)	113.7	113.9	113.9	116.6	116.7

TABLE II  
(Continued)

Compound	<i>IIa</i>	<i>IIIa</i>	<i>IIIb</i>	<i>IIIc</i>	<i>IIId</i>
Torsion angles (°)					
H—C(a)—C(5)—C(4)	0 0	0·0	0·0	59·8	59·7
H'—C(a)—C(5)—C(4)	—120·9	—121·0	—121·0	180 0	180 0
H''—C(a)—C(5)—C(4)	120·9	121·0	121·0	—59·8	—59·7
H—C(b)—C(5)—C(4)	120·8	—59·4	—59·4	59·3	59·3
H'—C(b)—C(5)—C(4)	0·0	180·0	180·0	180 0	180 0
H''—C(b)—C(5)—C(4)	—120·8	59·4	59·4	—59·3	—59·3
C(a)—C(5)—C(4)—C(3)	0·0	0·0	0·0	0·0	0·0
C(b)—C(5)—C(4)—C(3)	180·0	180·0	180·0	180·0	180 0

<sup>a</sup> The other atoms lie in the same plane.

considerable similarity to the results obtained in analogous way for 2,4-pentadienal conformers<sup>9</sup>. Certain differences are only encountered in detail values of valence angles of skeletal hydrogen bonds and valence angle C(4)—C(5)—C(6). Thus, introduction of methyl substituent should not exert any distinct influence on molecular structures of the forms *IIa*—*IIId* (R = CH<sub>3</sub>). To compare the effect of quality of the CNDO/2 wave function on the molecular structures obtained by the optimization, we carried out MNDO optimization of the heterocycle *I* (R = CH<sub>3</sub>) and the most energy-preferred conformer *IIb* (R = CH<sub>3</sub>). The structural parameters obtained by the two approaches are compared in Table III. The results show that the molecule of *I* (R = CH<sub>3</sub>) exists, according to the results of CNDO/2 optimization procedure, in boat conformation similar to that of the unsubstituted 2*H*-pyran molecule<sup>9</sup>.



Introduction of 2,2-methyl groups also results in a certain lengthening of O(1)—C(2) and C(2)—C(3) bonds. At the same time the valence angle O(1)—C(2)—C(3) is decreased, and C(6)—O(1)—C(2) is increased. Thus, the presence of the two methyl groups can be considered a stabilizing factor, as their introduction to 2 position removes, to some extent, the considerable deformation of the valence angle calculated for the tetrahedral centre in 2H-pyran<sup>9</sup>. Data of Table III reveal that the MNDO optimization gives more realistic, lower values of C—H bond lengths, the values of C—C bonds being, on the contrary, systematically higher. The value of CO bond of structure *I* (R = CH<sub>3</sub>) is higher, whereas that of *I*b (R = CH<sub>3</sub>) is lower (Table III). As far as values of valence angles are concerned, the two methods give identical semiquantitative trends, differing only in detail values by maximum of  $\pm 2^\circ$ . A substantially different situation is seen in values of dihedral angles which affect most the overall shape of the molecules. In the case of the heterocycle *I* (R = CH<sub>3</sub>) the two optimizations give practically identical boat structures with deviations below  $\pm 2^\circ$ , whereas for the model *I*b (R = CH<sub>3</sub>) the CNDO/2 gradient optimization leads to fully planar conformation, and the result of MNDO optimization rather reminds of a distorted helix.

#### Energy Characteristics

Table IV compares the calculated total and relative energies ( $E_{\text{tot}}$  and  $E_{\text{rel}}$ ) for all the types of bases of AOs. The values of CNDO/2, STO-3G, and 4-31G total energies were used for prediction of thermodynamic stability of structures *I*–*III*. Similar to the unsubstituted substances<sup>9</sup>, CNDO/2 and STO-3G give qualitatively different edicts, preferring 2,2-dimethyl-2H-pyran (*I*) to all conformers of 5-methyl-2,4-hexadienal (*IIa*–*IIIb*). CNDO/2 presumes the following stability order:  $I > IIb > IIa > IIIb > IIId > IIIa > IIIc$ . The STO-3G calculation leads to similar conclusions, the structure *IIIa* being, however, preferred:  $I > IIb > IIa > IIIa > IIIb > IIId > IIIc$ . In spite of detailed differences in the order, the energy difference is obviously greater for the valence isomerism  $I \rightleftharpoons II$  or  $III$  than for  $II \rightleftharpoons III$ . On the contrary, the 4-31G total energies give the following stability sequence:  $IIb > IIIb > IIIa > IIa > I > IIId > IIIc$ , hence the isomerism (*A*) can, in our case, be formulated most probably as  $IIb \rightleftharpoons IIa \rightleftharpoons I$  in favour of the open forms *II*. Similarly, the MNDO total energies of the MNDO-optimized models prefer structure *IIb* (R = CH<sub>3</sub>) to cyclic structure *I* (R = CH<sub>3</sub>) by 5.90 kJ mol<sup>-1</sup>. The different results of 4-31G and MNDO calculations *vs* those of CNDO/2 and STO-3G are obviously due to insufficient diffusivity of the latter bases of AOs for description of  $\pi$  structure mainly of the conformers of 5-methyl-2,4-hexadienal (*IIa*–*IIIb*). From the 4-31G values of relative energies of *I* to *III* structures it follows, of course, that energy difference between the open forms *IIa*–*IIIb* (R = CH<sub>3</sub>) and pyran skeleton *I* (R = CH<sub>3</sub>) is distinctly lower than that between the corresponding non-methylated compounds<sup>9</sup>.

TABLE III

The structural parameters of models *I* and *IIb* ( $R = CH_3$ ) obtained by CNDO/2 and MNDO gradient optimization. The values of bond lengths are given in pm, the angles are in degrees

Bond	CNDO/2	MNDO	Valence angle	CNDO/2	MNDO	Torsion angle	CNDO/2	MNDO
2,2-Dimethyl-2H-pyran ( <i>I</i> )								
O(1)—C(2)	140.4	143.0	O(1)—C(2)—C(3)	115.8	113.0	O(1)—C(2)—C(3)—C(4)	2.8	-1.0
C(2)—C(3)	147.1	153.1	C(2)—C(3)—C(4)	123.2	122.4	C(2)—C(3)—C(4)—C(5)	0.3	-0.3
C(3)—C(4)	133.6	135.3	C(3)—C(4)—C(5)	118.3	119.2	C(3)—C(4)—C(5)—C(6)	-1.5	0.3
C(4)—C(5)	143.8	145.6	C(4)—C(5)—C(6)	118.0	118.9	C(4)—C(5)—C(6)—O(1)	-0.5	1.0
C(5)—C(6)	133.5	136.3	C(5)—C(6)—O(1)	126.1	123.6	C(5)—C(6)—O(1)—C(2)	3.8	-2.5
C(6)—O(1)	136.0	135.4	C(6)—O(1)—C(2)	118.6	122.7	C(6)—O(1)—C(2)—C(3)	-4.6	2.3
C(a)—C(2)	147.9	156.5	C(a)—C(2)—O(1)	108.2	106.8	C(a)—C(2)—O(1)—C(6)	115.1	-118.4
C(b)—C(2)	147.9	156.5	C(b)—C(2)—O(1)	107.5	106.7	C(b)—C(2)—O(1)—C(6)	-124.5	123.0
H(3)—C(3)	111.7	109.0	H—C(a)—C(2)	113.2	107.6	H—C(a)—C(2)—O(1)	59.5	-58.3
H(4)—C(4)	111.7	109.0	H'—C(a)—C(2)	112.3	107.6	H'—C(a)—C(2)—O(1)	-60.1	62.3
H(5)—C(5)	111.4	108.7	H''—C(a)—C(2)	112.4	107.5	H''—C(a)—C(2)—O(1)	179.9	-178.2
H(6)—C(6)	111.9	109.7	H—C(b)—C(2)	112.5	111.4	H—C(b)—C(2)—O(1)	66.1	-65.9
H—C(a)	112.2	110.8	H'—C(b)—C(2)	113.0	111.9	H'—C(b)—C(2)—O(1)	-53.5	54.7
H'—C(a)	112.1	110.9	H''—C(b)—C(2)	112.4	110.5	H''—C(b)—C(2)—O(1)	-173.7	174.6
H''—C(a)	111.9	110.9	H(3)—C(3)—C(4)	121.6	121.6	H(3)—C(3)—C(4)—C(5)	-179.8	179.7
H—C(b)	112.1	110.8	H(4)—C(4)—C(5)	119.3	118.5	H(4)—C(4)—C(5)—C(6)	178.6	-179.9
H'—C(b)	112.1	110.8	H(5)—C(5)—C(6)	121.3	121.6	H(5)—C(5)—C(6)—O(1)	179.6	-179.6
H''—C(b)	111.9	110.9	H(6)—C(6)—O(1)	109.0	111.8	H(6)—C(6)—O(1)—C(2)	-176.7	177.6

5-Methyl-2,4-hexadienal (*Ifb*)

O—C(1)	126.6	122.2	O—C(1)—C(2)	126.4	125.6	C(3)—C(2)—C(1)—O	0.0	51.3
C(1)—C(2)	142.7	148.8	C(3)—C(2)—C(1)	125.5	128.5	C(4)—C(3)—C(2)—C(1)	0.0	0.9
C(2)—C(3)	134.2	134.7	C(4)—C(3)—C(2)	127.7	127.7	C(5)—C(4)—C(3)—C(2)	180.0	—112.7
C(3)—C(4)	143.1	147.2	C(5)—C(4)—C(3)	129.2	127.7	C(a)—C(5)—C(4)—C(3)	0.0	2.4
C(4)—C(5)	135.1	135.5	C(a)—C(5)—C(4)	124.8	124.1	C(b)—C(5)—C(4)—C(3)	180.0	—178.0
C(a)—C(5)	145.6	150.9	C(b)—C(5)—C(4)	121.5	120.7	H(1)—C(1)—C(2)—C(3)	180.0	—170.1
C(b)—C(5)	145.7	151.2	H(1)—C(1)—C(2)	115.7	113.3	H(2)—C(2)—C(1)—O	180.0	—130.4
H(1)—C(1)	112.5	111.2	H(2)—C(2)—C(1)	115.2	112.5	H(3)—C(3)—C(2)—C(1)	180.0	178.2
H(2)—C(2)	111.6	109.6	H(3)—C(3)—C(2)	117.3	118.3	H(4)—C(4)—C(3)—C(2)	180.0	—
H(3)—C(3)	112.2	108.8	H(4)—C(4)—C(3)	113.0	112.5	H—C(a)—C(5)—C(4)	0.0	69.0
H(4)—C(4)	112.2	109.8	H—C(a)—C(5)	114.9	113.3	H'—C(a)—C(5)—C(4)	0.0	0.5
H—C(a)	112.0	110.8	H'—C(a)—C(5)	111.2	110.7	H''—C(a)—C(5)—C(4)	—120.9	120.6
H'—C(a)	112.1	111.0	H''—C(a)—C(5)	111.2	110.7	H—C(b)—C(5)—C(4)	120.9	—119.7
H''—C(a)	112.1	111.1	H—C(b)—C(5)	114.4	110.8	H'—C(b)—C(5)—C(4)	120.8	—119.8
H—C(b)	112.1	111.0	H'—C(b)—C(5)	111.4	112.8	H''—C(b)—C(5)—C(4)	0.0	0.4
H'—C(b)	112.0	110.9	H''—C(b)—C(5)	111.4	110.8	H(2)—C(2)—C(1)—H(1)	—120.8	120.5
H''—C(b)	112.1	111.0	C(a)—C(5)—C(b)	113.7	115.2	H(3)—C(3)—C(2)—H(2)	0.0	48.3
							0.0	—0.1

TABLE IV  
Comparison of total and relative energies of the structures I–III

Compound	$-E_{\text{tot}}^a$				$E_{\text{rel}}^b$ , kJ mol $^{-1}$			
	STO-3G $^b$	4-31G $^c$	STO-3G $^{b,d}$	4-31G $^{b,d}$	CNDO/2	STO-3G $^b$	4-31G $^c$	4-31G $^{b,d}$
I	341.437536	345.195989 345.195903 $^b$	264.285447	267.235607	0.0	0.0	11.5 11.7 $^b$	27.1
IIa	341.388163	345.199082	264.231493	267.241367	651.5	129.8	3.4	11.8
IIb	341.388518	345.200356	264.232064	267.242993	644.4	128.8	0.0	7.6
IIIa	341.388017	345.199859	264.234765	267.245916	657.6	130.1	1.3	0.0
IIIb	314.387518	345.199947	264.234145	267.245289	625.8	131.5	1.1	1.6
IIIc	341.363065	345.174306	264.231891	267.240824	658.9	195.7	68.5	13.4
IIId	341.378484	345.189097	264.231089	267.239834	655.4	155.2	29.6	16.0

$^a$  The values are given in dimensionless units  $E = E_{\text{tot}}/E_{\text{H}}$ , where  $E_{\text{H}} = 2.628.1$  kJ mol $^{-1}$ ;  $^b$  the calculation involves two-electron integrals greater than  $1 \cdot 10^{-6}$ ;  $^c$  the calculation involves two-electron integrals greater than  $1 \cdot 10^{-5}$ ;  $^d$ , the values for non-substituted structures.



Table V gives values of 4–31G energies of frontier orbitals of the models *I–III* ( $R = \text{CH}_3$ ). Compared with the non-substituted molecule of 2*H*-pyran itself and with its non-cyclic valence isomers<sup>9</sup>, introduction of 2,2-dimethyl groups in the derivative *I* only results in non-distinct increase of both the HOMO and LUMO energies. Analogous comparison of energy values of frontier MOs of 5-methyl-2,4-hexadienal conformers *IIa–IIIc* with those of 2,4-pentadienal itself<sup>9</sup> shows a more distinct lowering of the HOMO energies and increase of the LUMO energies. The molecule *I* tends to electron-donor interactions, and all the conformers *IIa–IIIc* tend to electron-acceptor interactions, which is similar to the behaviour of the unsubstituted system. The nodal properties of the frontier MOs of all the systems remain practically identical with those of the non-substituted compounds<sup>9</sup>. The HOMO of the pyran model *I* is of pseudo- $\pi$ -type with distinct bonding participation of 2s orbitals of the both methyl carbon atoms with nodal planes perpendicular to the bonds O(1)–C(2), C(2)–C(3), C(4)–C(5), C(6)–O(1), which indicates C-hyperconjugation. Similarly, the LUMO is again of  $\pi$ -type with analogous antibonding antisymmetrical participation of 2s orbitals of the methyl carbon atoms and with nodal planes perpendicular to the bonds C(2)–C(3), C(3)–C(4), C(5)–C(6), C(6)–O(1). Table VI gives the expansion coefficients of AOs in the HOMO and the LUMO of the model compound *I* ( $R = \text{CH}_3$ ) along with those of the energetically most favourable conformer *IIb* ( $R = \text{CH}_3$ ).

### Charge Distribution

The values of STO-3G  $\sigma$  and  $\pi$  charge populations of the open forms *IIa–IIIc* ( $R = \text{CH}_3$ ) show a rather non-distinct dependence on conformation relations. All the structures exhibit characteristic alternation of the  $\pi$  charges along the skeleton, whereas the charges  $\sigma$  are always negative except for C(1) centre. Hence, it can be

TABLE V  
The 4–31G energies<sup>a</sup> of the frontier orbitals of structures *I–III* ( $R = \text{CH}_3$ )

Compound	<i>I</i>	<i>IIa</i>	<i>IIb</i>	<i>IIIa</i>	<i>IIIb</i>	<i>IIIc</i>	<i>IIIc</i>
HOMO <sup>b</sup>	7.79	8.69	8.48	8.60	8.50	8.56	8.54
LUMO <sup>b</sup>	3.62	1.60	1.61	1.59	1.62	1.59	1.54

<sup>a</sup> The calculation involved the two-electron integrals higher than  $1 \cdot 10^{-5}$ ; <sup>b</sup> the values are given in dimensionless units  $E = E_n/h$ , where  $h = 96.4867 \text{ kJ mol}^{-1}$ .

stated that introduction of the two methyl groups in C(5) position of 2,4-pentadienal causes no distinct change in character of charge population. A somewhat different situation is presented in Table VII for 4-31G model of the heterocycle *I* ( $R = CH_3$ ). In this case obviously the introduction of methyl groups in 2 position changes the O(1)-C(2) bond strength, because the original considerably repulsive interaction of  $\pi$  charges at the O(1) and C(2) centres of the unsubstituted skeleton<sup>9</sup> is transformed into an attractive interaction of negative  $\pi$  charge at O(1) and positive  $\pi$  charge

TABLE VI

LCAO expansions for the frontier 4-31G MOs of *I* and *Iib* molecules<sup>a</sup>. Only given are the members with the expansion coefficients above 0.1; meaning of the symbols for AOs:  $p_z = 2p_z(I)$ ,  $p'_z = 2p_z(O)$ ,  $S = 2s(I)$ ,  $S' = 2s(O)$ ,  $s = 1s(I)$ ,  $s' = 1s(O)$

HOMO	LUMO
2,2-Dimethyl-2 <i>H</i> -pyran ( <i>I</i> )	
0.2298 $p_zO(1)$ + 0.2457 $p'_zO(1)$	0.1380 $p_zO(1)$ + 0.1845 $p'_zO(1)$
- $p_zC(2)$	$p_zC(2)$
0.2724 $p_zC(3)$ + 0.2898 $p'_zC(3)$	-0.2828 $p_zC(3)$ - 0.5270 $p'_zC(3)$
0.1932 $p_zC(4)$ + 0.2229 $p'_zC(4)$	0.2264 $p_zC(4)$ + 0.4152 $p'_zC(4)$
-0.2583 $p_zC(5)$ - 0.2980 $p'_zC(5)$	0.1658 $p_zC(5)$ + 0.2975 $p'_zC(5)$
-0.2567 $p_zC(6)$ - 0.2340 $p'_zC(6)$	-0.3006 $p_zC(6)$ - 0.5063 $p'_zC(6)$
- 0.1348 $SC(a)$	0.1574 $SC(a)$
0.1278 $SC(b)$	- 0.1479 $SC(b)$
	-0.1909 $sH(a)$
	0.1822 $sH(b)$
5-Methyl-2,4-hexadienal ( <i>Iib</i> )	
0.1791 $p_zO$ + 0.1698 $p'_zO$	-0.2315 $p_zO$ - 0.2934 $p'_zO$
- $p_zC(1)$	0.2294 $p_zC(1)$ + 0.2883 $p'_zC(1)$
-0.2776 $p_zC(2)$ - 0.3092 $p'_zC(2)$	0.1688 $p_zC(2)$ + 0.2933 $p'_zC(2)$
-0.1338 $p_zC(3)$ - 0.1298 $p'_zC(3)$	-0.2727 $p_zC(3)$ - 0.4351 $p'_zC(3)$
0.2589 $p_zC(4)$ + 0.2754 $p'_zC(4)$	-0.0789 $p_zC(4)$ - 0.1183 $p'_zC(4)$
0.2617 $p_zC(5)$ + 0.2717 $p'_zC(5)$	0.2506 $p_zC(5)$ + 0.3585 $p'_zC(5)$
- $SC(a)$	$SC(a)$
$SC(b)$	- $SC(b)$
	-0.1632 $sH(a)$
	0.1632 $sH''(a)$
	-0.1324 $sH(b)$
	0.1324 $sH''(b)$

<sup>a</sup> The CNDO/2-optimized geometries.

TABLE VII  
Comparison of total,  $\sigma$  and  $\pi$  STO-3G charge distributions of the CNDO/2-optimized models of structures *I* and *IIb* ( $R = CH_3$ ). Upper and lower specifications of position relate to compounds *I* and *IIb*, respectively

$Q_i$	O(1)		C(2)		C(3)		C(4)		C(5)		C(6)		$C^a$		H(3)		H(4)		H(5)		H(6)		$H^a$	
	O	C(1)	C(2)	C(3)	C(4)	C(3)	C(4)	C(5)	C(4)	C(5)	C(6)	C(5)	H(1)	H(2)	H(3)	H(4)	H(3)	H(4)	H(5)	H(6)				
Total	-0.255	0.149	-0.068	-0.060	-0.060	-0.060	-0.060	-0.060	-0.116	0.088	-0.159	0.055	0.061	0.060	0.072	0.054								
$\sigma$	0.598	0.123	-0.038	-0.063	-0.063	-0.063	-0.063	-0.063	-0.002	0.066	-0.187	—	—	—	—	—	—	—	—	—	—	—	—	—
$\pi$	-0.853	0.026	-0.029	0.003	0.003	0.003	0.003	0.003	-0.114	0.022	0.029	—	—	—	—	—	—	—	—	—	—	—	—	—
2,2-Dimethyl-2 <i>H</i> -pyran ( <i>I</i> )																								
5-Methyl-2,4-hexadienal ( <i>IIb</i> )																								
Total	-0.213	0.111	-0.096	-0.023	-0.084	0.035	-0.167	0.043	0.060	0.059	0.079	0.061	0.060	0.059	0.079	0.061								
$\sigma$	-0.077	0.030	-0.034	-0.099	-0.044	-0.024	-0.153	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
$\pi e$	-0.136	0.081	-0.062	0.076	-0.040	0.059	-0.014	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

<sup>a</sup> Average value for the two methyl groups.

at C(2). On the contrary, however, the introduction of two methyl groups in 2 position results in increased repulsion interaction of  $\sigma$ -charge densities of these centres, hence the final effect on the O(1)--C(2) bond strength is a result of mutual compensation of  $\sigma$  and  $\pi$  charge distributions. The introduction of two methyl groups in C(2) position of 2*H*-pyran skeleton can be considered a rather stabilizing factor which could shift the equilibrium (A) in favour of the cyclic isomer. In contrast to unequivocal preference of structure I (R = CH<sub>3</sub>) following from the less perfect CNDO/2 and STO-3G calculations, however, the energy data obtained by the more perfect MNDO and 4-31G procedures do not confirm this preference and, moreover, show substantially lower energy differences between the individual forms of the considered valence isomer I-III (R = CH<sub>3</sub>). Furthermore, of course, any more precise prognosis would require additional calculation of corrections for correlation energy and zero point.

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