MO STUDY OF 2,2,4-TRIMETHYL-2*H*-PYRAN, THE SIMPLEST STABLE 2*H*-PYRAN DERIVATIVE

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On the basis of MNDO optimized molecular geometries of the title compound *I* and its acyclic valence tautomers *II* and *III* it is demonstrated that the ability to isolate heterocyclic form *I* can be interpreted by its relatively lowest SCF-molecular energy calculated in MNDO or 4-31G, resp., orbital bases. Quantum chemical data are discussed in connection with the more general relation between the stability of 2*H*-pyran cycle and structural factors causing non-planarity of the equilibrium geometries of non-cyclic tautomeric structures.

A number of experimental results shows[1] that the stability of 2*H*-pyran derivatives is primarily limited by their valence tautomerism with respective *cis*-2,4-dienones. As these systems rapidly establish equilibrium, thermodynamic factors are decisive for detection of the heterocyclic tautomer. Non-substituted 2*H*-pyran has thus so far not been proved experimentally and owing to this fact its energy stability has been the subject of several MO quantum chemical studies[2-5]. The results of theses studies, with respect to perfection of MO approximations were somewhat contradictory and the final theoretical justification of the possibility to prove experimentally the existence of 2*H*-pyran molecule can not be done. The calculated SCF-molecular energies of 2*H*-pyran and of *cis*-2,4-pentadienal prefer either cyclic or acyclic valence tautomer. Calculations based on the CNDO/2 gradient optimized molecular geometries[4] preferentially lead to the use of the cyclic forms CNDO/2 or STO-3G, resp., energies, while use of 4-31G energy leads to the preference of planar acyclic tautomer.

On the other hand, MINDO/3 optimized geometries[5] using MINDO/3 heats of formation again prefer cyclic tautomer to a non-planar acyclic one. The non-planarity of the last mentioned tautomer is rather difficult to explain by more known nonbonded interactions. Nevertheless the most probable is the artifact of the used optimization procedure[6] and, thus, the conclusions[5] concerning the relative stability of both tautomers and energy barriers between them are not very convincing. Therefore, it is no doubt that the further strategy of MO calculations of 2*H*-pyran itself will be directed to the use of a more sofisticated non-empirical optimization, or possibly even to the study of correlation energy and zero point energy effects. These plans are gradually put to test in our laboratory and the results will be reported elsewhere.

Simultaneously with the above mentioned study on unsubstituted 2*H*-pyran it seems necessary to follow an alternative aspect, as well that is how thus far less demanding MO methods investigated express the effect of various substituents on the relative stability of 2*H*-pyran derivatives. The current MO studies are limited only to 2,2-dimethyl-2*H*-pyran[7] and to 2-amino-2*H*-pyran[5,8]. They all suggest the presence of some stabilizing effects of the considered substitution in favour of the heterocyclic form, the existence of which has not yet been successed fully proved[1].

The aim of this communication is a semiempirical and non-empirical MO study of a molecular and electronic structure of 2,2,4-trimethyl-2*H*-pyran (*I*), the simplest heterocycle of this class of compounds that can be isolated.

CALCULATIONS

The molecular geometries of structures *I*–*III* were obtained by means of MNDO optimization[9-11] with respect to all degrees of freedom. An idealized structure[12], in analogy to the results of optimization of 2,2-dimethyl-2*H*-pyran (see ref.[7]), was chosen as a starting geometry for the optimization of cyclic form *I*. Idealized geometries with non-planar arrangement were again used in the case of the conformers of 3,5-dimethyl-2,4-hexadienal, *II* and *III*. This choice was conducted in such a way so that the end fragments of the molecule mutually exhibited an assymetric torsion, formed by its deviation from the plane of the central ethylene unit about 5°.

TABLE I

Comparison of structural parameters of acyclic valence isomers *II*–*III* obtained by MNDO optimization

Parameter	Compound					
	IIa	*IIb*	*IIIa*	*IIIb*	*IIIc*	*IIId*
Bond lengths, pm						
O—C(1)	122·2	122·4	122·2	122·3	122·1	122·4
C(1)—C(2)	148·6	148·9	149·2	148·5	149·0	148·9
C(2)—C(3)	135·8	135·7	135·4	135·8	135·4	135·7
C(3)—C(4)	148·3	148·3	148·5	148·8	148·6	148·6
C(4)—C(5)	135·5	135·5	135·5	125·4	135·6	135·4
C(*a*)—C(5)	150·9	151·0	151·3	151·1	151·1	151·1
C(*b*)—C(5)	151·1	151·1	150·8	150·9	151·0	150·9
C(*c*)—C(5)	151·5	151·4	151·0	151·1	151·1	151·1
H(1)—C(1)	111·3	111·0	111·2	111·3	111·2	111·0
H(2)—C(2)	109·7	109·7	109·6	109·8	109·6	109·7
H—C(*c*)	110·9	110·9	111·0	110·9	110·9	110·9
H′—C(*c*)	111·0	111·0	111·0	110·9	111·0	111·0
H″—C(*c*)	111·0	111·0	110·9	111·0	111·0	111·0
H(4)—C(4)	109·8	109·8	109·8	109·8	109·8	109·8
H—C(*b*)	111·0	110·9	110·8	110·9	110·9	110·9
H′—C(*b*)	111·1	111·0	111·1	111·0	111·1	110·9
H″—C(*b*)	110·9	111·0	111·0	111·0	110·9	111·1
H—C(*a*)	110·9	110·9	110·9	111·1	110·9	110·9
H′—C(*a*)	111·1	111·1	111·0	110·9	111·0	111·0
H″—C(*a*)	111·0	111·0	111·1	110·9	111·0	111·0

TABLE I

(*Continued*)

Parameter	Compound					
	IIa	*IIb*	*IIIa*	*IIIb*	*IIIc*	*IIId*
Bond angles, deg						
O—C(1)—C(2)	126·8	123·2	123·9	126·9	125·6	123·2
C(1)—C(2)—C(3)	130·0	127·0	127·0	130·6	128·9	127·5
C(2)—C(3)—C(4)	124·1	123·7	119·9	119·2	119·9	119·6
C(3)—C(4)—C(5)	128·3	128·4	128·7	128·5	128·4	128·4
C(4)—C(5)—C(*a*)	123·5	123·4	119·6	120·6	120·6	120·6
C(4)—C(5)—C(*b*)	120·5	120·6	124·3	123·8	123·5	123·6
C(*c*)—C(3)—C(4)	115·7	115·8	115·9	115·1	115·5	115·3
H(1)—C(1)—C(2)	112·8	116·5	114·9	112·8	113·2	116·7
H(2)—C(2)—C(3)	118·6	114·0	112·9	111·2	111·3	113·8
H(4)—C(4)—C(3)	111·7	111·7	111·6	111·5	111·6	111·7
H—C(*a*)—C(5)	112·9	112·8	113·1	112·8	112·2	112·1
H′—C(*a*)—C(5)	110·8	110·8	110·2	111·0	110·6	112·1
H″—C(*a*)—C(5)	110·7	110·7	111·3	110·6	111·9	110·5
H—C(*b*)—C(5)	112·4	112·4	112·6	110·1	112·8	112·8
H′—C(*b*)—C(5)	111·0	110·9	111·4	111·9	110·6	110·7
H″—C(*b*)—C(5)	111·5	111·5	110·7	112·7	111·0	110·8
H″—C(*c*)—C(3)	111·0	110·9	112·1	110·7	110·9	110·9
H′—C(*c*)—C(3)	110·7	110·8	111·4	111·5	111·4	111·3
H—C(*c*)—C(3)	112·5	112·4	110·7	112·0	112·0	112·1
Dihedral angles, deg						
C(3)—C(2)—C(1)—O	−12·4	172·7	121·6	−13·9	−56·4	182·7
C(4)—C(3)—C(2)—C(1)	−1·1	−1·6	177·1	177·5	183·9	177·3
C(5)—C(4)—C(3)—C(2)	97·7	95·5	88·6	88·7	−84·1	84·0
C(*a*)—C(5)—C(4)—C(3)	−1·1	−0·8	180·1	179·5	180·4	181·5
C(*b*)—C(5)—C(4)—C(3)	178·9	178·8	0·7	0·5	0·6	0·3
C(*c*)—C(3)—C(4)—C(5)	−85·5	−87·4	−92·9	−93·8	98·7	−98·8
H(1)—C(1)—C(2)—C(3)	167·9	−7·4	−60·4	−12·8	125·4	2·8
H(2)—C(2)—C(1)—O	168·7	−6·9	−59·2	166·6	125·5	2·5
H(4)—C(4)—C(3)—C(2)	−83·1	−85·6	−91·5	−91·8	96·8	−95·9
H—C(*b*)—C(5)—C(4)	0·1	0·2	−16·7	−6·4	195·5	160·8
H′—C(*b*)—C(5)—C(4)	120·3	120·3	103·5	233·5	75·9	40·9
H″—C(*b*)—C(5)—C(4)	240·1	240·1	223·2	113·6	315·5	280·5
H—C(*a*)—C(5)—C(4)	184·8	186·7	188·8	88·9	−7·2	1·6
H′—C(*a*)—C(5)—C(4)	65·1	67·0	308·8	208·5	112·9	121·7
H″—C(*a*)—C(5)—C(4)	304·7	306·5	68·8	328·6	232·8	241·6
H—C(*c*)—C(3)—C(4)	178·6	177·0	113·1	11·4	7·8	6·1
H′—C(*c*)—C(3)—C(4)	58·8	57·1	233·5	131·1	127·4	125·9
H″—C(*c*)—C(3)—C(4)	298·9	297·3	353·1	251·8	247·9	246·4

Non-empirical calculations in the STO-3G and 4-31G bases sets, resp., were carried out with the modified version of Gaussian 76 program (see ref.[13]). The program was on one hand enlarged to enable the calculations of the larger molecular systems and on the other hand its SCF section was chiefly rewritten to ASSEMBLER of computer Cyber 172 using several sub-programs of the set of programs Phantom[14]. The mentioned modifications led to an approximately triple reduction of the computing time. For calculation of STO-3G and 4-31G total eneries only two-electron integrals with absolute value greater then $1 \cdot 10^{-6}$ were used.

RESULTS AND DISCUSSION

Molecular Structure

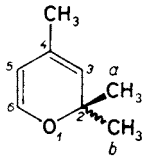
Structural parameters of 2,2,4-trimethyl-2*H*-pyran (*I*) as well as of six conformers of acyclic tautomer – 3,5-dimethyl-2,4-hexadienal (*II* and *III*) are given in Table I

TABLE II

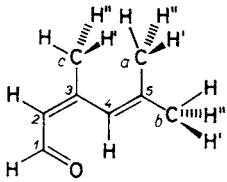
MNDO structural parameters of 2,2,4-trimethyl-2*H*-pyran (*I*)

Bond length, pm		Bond angles, deg		Dihedral angles, deg	
O—C(2)	142·8	O—C(2)—C(3)	113·3	O—C(2)—C(3)—C(4)	0·0
C(2)—C(3)	153·1	C(2)—C(3)—C(4)	123·5	C(2)—C(3)—C(4)—C(5)	0·1
C(3)—C(4)	136·1	C(3)—C(4)—C(5)	117·2	C(3)—C(4)—C(5)—C(6)	−0·1
C(4)—C(5)	146·5	C(4)—C(5)—C(6)	120·0	C(4)—C(5)—C(6)—O	0·1
C(5)—C(6)	136·2	C(5)—C(6)—O	123·9	C(5)—C(6)—O—C(2)	−0·1
C(6)—O	135·3	C(6)—O—C(2)	122·2	C(6)—O—C(2)—C(3)	0·0
C(4)—C(*c*)	150·5	C(*a*)—C(2)—C(3)	109·5	C(*a*)—C(2)—C(3)—C(4)	119·1
C(2)—C(*a*)	156·5	C(*b*)—C(2)—C(3)	109·6	C(*b*)—C(2)—C(3)—C(4)	240·9
C(2)—C(*b*)	156·5	C(*c*)—C(4)—C(5)	120·2	C(*c*)—C(4)—C(5)—C(6)	179·8
H(3)—C(3)	109·1	H(3)—C(3)—C(4)	121·7	H(3)—C(3)—C(4)—C(5)	0·1
H(5)—C(5)	108·8	H(5)—C(5)—C(4)	119·8	H(5)—C(5)—C(4)—C(3)	180·0
H(6)—C(6)	109·7	H(6)—C(6)—C(5)	124·4	H(6)—C(6)—C(5)—C(4)	180·1
H—C(*c*)	110·9	H—C(*c*)—C(4)	112·5	H—C(*c*)—C(4)—C(5)	4·6
H′—C(*c*)	111·0	H′—C(*c*)—C(4)	111·9	H′—C(*c*)—C(4)—C(5)	124·7
H″—C(*c*)	111·1	H″—C(*c*)—C(4)	110·8	H″—C(*c*)—C(4)—C(5)	244·6
H—C(*a*)	110·9	H—C(*a*)—C(2)	111·4	H—C(*a*)—C(2)—C(3)	−58·1
H′—C(*a*)	110·9	H′—C(*a*)—C(2)	110·6	H′—C(*a*)—C(2)—C(3)	61·6
H″—C(*a*)	110·9	H″—C(*a*)—C(2)	111·8	H″—C(*a*)—C(2)—C(3)	181·4
H—C(*b*)	110·9	H—C(*b*)—C(2)	111·4	H—C(*b*)—C(2)—C(3)	58·4
H′—C(*b*)	110·8	H′—C(*b*)—C(2)	111·8	H′—C(*b*)—C(2)—C(3)	178·9
H″—C(*b*)	110·8	H″—C(*b*)—C(2)	111·6	H″—C(*b*)—C(2)—C(3)	298·8

and Table II, resp. From given values it follows that the MNDO model of pyran *I* exhibits practically identical structural parameters as its simpler analogue, *e.g.* 2,2-dimethyl-2*H*-pyran[7]. Molecule *I* according to the MNDO optimization exhibits no anomal structural phenomena, as far as confirmation is concerned it is practically planar.



I



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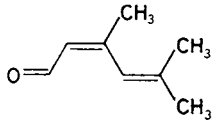

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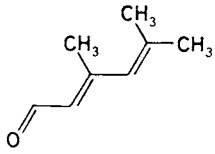

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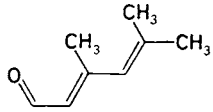

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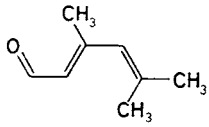
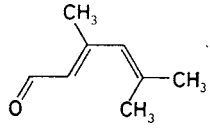


III c



III d

MNDO models of *Z*-conformer *IIb* and (*Z*)-5-methyl-2,4-hexadienal (ref.[7]) differ only slightly in the values of bond lengths and of bond angles. Some dihedral angles for the optimization of molecular geometries *II* and *III*, however, point to the distinct breakage of the coplanarity of π-electron systems of double bonds C=C. Above all both *Z*-conformers *IIa,b* are in equilibrium molecular geometry very strongly turned around the bond C(3)—C(4), as can be seen from the absolute values of the dihedral angles C(5)—C(4)—C(3)—C(2), C(*c*)—C(3)—C(4)—C(5), and H(4)—C(4)—C(3)—C(2), respectively, in the range of 83·1° and 97·4°. There is no doubt that this is the effect of nonbonded interaction between groups $CH_3(3)$ and $CH_3(5)$. In MNDO models of *E*-conformers *IIIa – d* the case is analogous to that of *IIa,b*.

MNDO, STO-3G, and 4-31G total energies of MNDO optimized model structures are summarized in Table III. All presented types of calculation, including MNDO heats of formation, point at higher thermodynamic stability of cyclic form *I* relative to all types of open forms *II* and *III*, resp. Introduction of the methyl group to position 4 results in increased energy differences between pyran *I* and its acyclic valence tautomers, as can be seen from the comparison with analogous calculations of 2,2′-dimethyl-2*H*-pyran and its acyclic tautomers[7]. Detailed comparison of energy differences of open forms *II* and *III* points to quite identical results of both non-empirical bases sets (STO-3G, 4-31G). On the other hand, however, MNDO total energies lead to very different order, although with very small energy differences between respective conformers.

TABLE III

Comparison of total and relative energies of structures *I*—*III*

Compound	MNDO		STO-3G		4-31G	
	$-E^a_{tot}$	E^c_{rel}	$-E^b_{tot}$	E^c_{rel}	$-E^b_{tot}$	E^c_{rel}
I	1 514·8393	0·0	380·03974	0·0	384·18794	0·0
IIa	1 514·8030	3·5	379·97934	158·7	384·17485	34·4
IIb	1 514·8162	2·2	379·98182	152·2	384·18074	18·9
IIIa	1 514·8234	1·5	379·97368	173·6	384·16865	50·7
IIIb	1 514·8018	3·6	379·98051	155·7	384·17922	22·9
IIIc	1 514·8306	0·8	379·97597	167·6	384·17208	41·7
IIId	1 514·7979	4·0	379·98150	153·1	384·17973	21·6

[a] The values are given in dimensionless units defined as $E = E_{tot}/h$, where $h = 96{\cdot}4867$ kJ mol^{-1}; [b] the values are given in dimensionless units defined as $E = E_{tot}/k$, where $k = 2\,628{\cdot}1$ kJ mol^{-1}; [c] the values are given in kJ mol^{-1}.

TABLE IV

4-31G HOMO and LUMO orbital energies[a] of the structures *I*—*III*

Structure	*I*	*IIa*	*IIb*	*IIIa*	*IIIb*	*IIIc*	*IIId*
HOMO	7·49	8·99	9·50	9·28	9·39	9·23	9·38
LUMO	3·49	2·51	2·53	3·12	2·50	3·00	2·41

[a] The values are given in dimensionless units defined as $E = E_n/h$, where $h = 96{\cdot}4867$ kJ mol^{-1}.

4-31G energies of frontier HOMO and LUMO orbitals of structures *I*–*III* are given in Table IV. Comparison with analogous data for 2*H*-pyran and 2,4-pentadienal[4], as well as for 2,2-dimethyl-2*H*-pyran and conformers of 5-methyl-2,4-hexadienal[7] shows practically identical values in the case of the pyran skeleton (−7·79, 3·62 and −7·49, 3·49, resp.) of both 2,2-dimethyl and 2,2,4-trimethyl derivatives, while a slight increase of the energies of both HOMO and LUMO occurs at the transition to acyclic isomers *II* and *III*. Similarly, molecule *I* seems to be like a π-electron donor, as well as in the case of less substituted skeletons[4,7], while all conformers of *II* and *III* appear to be like π-electron acceptors.

TABLE V

LCAO coefficients of the canonical 4-31G MO structures *I* and *IIb*. Only coefficients with the absolute value greater than 0·1 are given. For the characterization of AO's the following symbols are used: $p_{x,y,z} = 2p_{x,y,z}(I)$, $p'_{x,x,z} = 2p_{x,y,z}(O)$, $S = 2s(I)$, $S' = 2s(O)$, $s = 1s(I)$, $s' = 1s(O)$

HOMO	LUMO
2,2,4-trimethyl-2*H*-pyran (*I*)	
$-0{\cdot}2205p_z$ O(1) $-0{\cdot}2385p'_z$ O(1)	$-0{\cdot}1446p_z$ O(1) $-0{\cdot}1956p'_z$ O(1)
$-0{\cdot}2874p_z$ C(3) $-0{\cdot}3065p'_z$ C(3)	$0{\cdot}2641p_z$ C(3) $+0{\cdot}4899p'_z$ C(3)
$-0{\cdot}1882p_z$ C(4) $-0{\cdot}2278p'_z$ C(4)	$-0{\cdot}2400p_z$ C(4) $-0{\cdot}3802p'_z$ C(4)
$0{\cdot}2483p_z$ C(5) $+0{\cdot}2961p'_z$ C(5)	$-0{\cdot}1523p_z$ C(5) $-0{\cdot}2827p'_z$ C(5)
$0{\cdot}2397p_z$ C(6) $+0{\cdot}2222p'_z$ C(6)	$0{\cdot}2975p_z$ C(6) $+0{\cdot}4958p'_z$ C(6)
$0{\cdot}1361S'$ C(*a*)	$-0{\cdot}1386S'$ C(*a*)
$-0{\cdot}1360S'$ C(*b*)	$0{\cdot}1377S'$ C(*b*)
	$0{\cdot}1669p'_z$ C(*c*)
	$0{\cdot}1554s'$ H(*a*)
	$0{\cdot}1547s'$ H(*b*)
	$-0{\cdot}2704s'$ H(*c*)
	$0{\cdot}2705s'$ H′(*c*)
3,5-dimethyl-2,4-hexadienal (*IIb*)	
$0{\cdot}2585p_x$ C(4) $+0{\cdot}2759p'_x$ C(4)	$0{\cdot}2739p_z$ O $+0{\cdot}3486p'_z$ O
$0{\cdot}2322p_y$ C(4) $+0{\cdot}2191p'_y$ C(4)	$-0{\cdot}2519p_z$ C(1) $-0{\cdot}3605p'_z$ C(1)
$0{\cdot}2459p_x$ C(5) $+0{\cdot}2441p'_x$ C(5)	$-0{\cdot}1671p_z$ C(2) $-0{\cdot}3136p'_z$ C(2)
$0{\cdot}1846p_y$ C(5) $+0{\cdot}1881p'_y$ C(5)	$0{\cdot}3203p_z$ C(3) $+0{\cdot}4718p'_z$ C(3)
$0{\cdot}1006s'$ H(*b*)	$0{\cdot}1049p'_z$ C(4)
$-0{\cdot}1080s'$ H′(*b*)	$-0{\cdot}2582S$ C(5)
$0{\cdot}1082p_y$ C(*c*)	$0{\cdot}1086p_x$ C(5)
	$0{\cdot}2373s'$ H(4)
	$0{\cdot}1070p'_z$ C(*c*)
	$0{\cdot}2362s'$ H(*c*)
	$-0{\cdot}2396s'$ H′(*c*)

The virial coefficients of 4-31G HOMO and LUMO orbitals of pyran *I* and 4-31G of preferred conformer of acyclic structure *IIb* are given in Table V. HOMO of pyran *I* is of the π-type with bonding antisymmetrical participation of 2*s* orbitals of carbon atoms of methyl groups in position 2 with nodal planes perpendicular to bonds O(1)—C(2), C(2)—C(3), C(4)—C(5), C(6)—O(1). Similarly LUMO is of the π-type with analogous antibonding antisymmetrical participation of mentioned 2*s* orbitals of methyl groups and with the nodal planes perpendicular to bonds C(2)—C(3), C(3)—C(4), C(5)—C(6), and C(6)—O(1). In the case of open form *IIb* HOMO is of the π-type of terminal α,α-dimethyl unit, while LUMO is again of the π-type with localization in the sphere of the aldehydic group.

TABLE VI

Comparison of the total, σ and partial π 4-31G charge distributions of MNDO optimized models *I* and *IIb*. The upper, respectively lower symbols represent structures *I* and *IIb*, resp.

Q_i	O(1) O	C(2) C(1)	C(3) C(2)	C(4) C(3)	C(5) C(4)	C(6) C(5)
			2,2,4-trimethyl-2*H*-pyran (*I*)			
Total	−0·776	0·248	−0·214	0·007	−0·297	0·270
σ	0·079	0·224	−0·139	−0·041	−0·141	0·193
π	−0·854	0·024	−0·074	0·048	−0·156	0·077
			3,5-dimethyl-2,4-hexadienal (*IIb*)			
Total	−0·571	0·345	−0·276	0·006	−0·235	0·030

TABLE VII

The comparison of 4-31G energetic changes ΔE for valence tautomerism (*A*) with dihedral angles Φ in molecules of acyclic tautomers calculated semiempirically

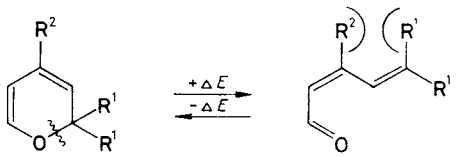
R^1	R^2	Φ, deg	ΔE, kJ mol^{-1}	Ref.
H	H	180·0	−19·5	4
CH_3	H	112·7	−11·5	7
CH_3	CH_3	97·7	+34·4	—[a]

[a] The presented work.

Charge Distribution

Values of σ and π charge distributions for pyran *I* and a total charge distribution for *Z*-conformer *IIb* are given in Table VI. Distribution in 4-31G model of *IIb* has the same characteristics as in other cases *IIa* and *IIIa – d*, *e.i.* a characteristic charge alternation, similar to the less substituted structures[7]. Also π-distribution of pyran *I* is almost identical to that of 2,2-dimethyl-2*H*-pyran[7]. On the other hand, lower values of corresponding σ-charges on O and C(2) atoms, *i.e.* +0·079 and +0·224 is the result of lower σ-repulsion between these atom centres in compound *I*. This finding may be interpreted in the terms of a stabilizing influence of 4-methyl group in heterocycle *I* on its electronic structure.

The confrontation of the above mentioned MNDO and 4-31G calculatins with analogous formerly published calculations[4,7] enables a deeper insight on the effect of substitution by methyl in valence tautomerism (*A*).



(*A*)

From Table VII it is obvious that the decrease in the value of the dihedral angle Φ in fragment C(5)—C(4)—C(3)—C(2) from 180° to 90° is accompanied by energetic destabilization of equilibrium molecular geometry of acyclic tautomer and following shift of equilibrium (*A*) to the left. The main cause of the changes of angle Φ is always an increasing steric interaction between substituents R^1 and R^2 in agreement with empirically founded results[1]. The changes in detailed σ-electron distribution in heterocyclic tautomers affecting the strength of bond O—C(2) is also an additional cause.

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