MO STUDY OF MOLECULAR AND ELECTRONIC STRUCTURE OF 2*H*- AND 4*H*-PYRANS

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CNDO/2, STO-3G and 4-31G MO calculations have been carried for the molecules *I—IV*. Their molecular and electronic structure is discussed with respect to relative stabilities of the respective compounds and valence isomerism $I \rightleftharpoons III$. Significance of application of the split-valence base in the *ab initio* MO calculations carried out is demonstrated.

The both unsubstituted pyrans *I* and *II* belong among basic ring systems of heterocyclic chemistry. Attempts of preparation of 2*H*-pyran (*I*) have been unsuccessful so far[1] due to its tendency to rapid isomerization to *cis*-2,4-pentadienal (*III*). On the contrary, the 4*H*-isomer *II* was prepared by several independent syntheses[2-4] and appears thus to be substantially more stable. With the aim of deeper understanding of the different stabilities of the said compounds *I* and *II* we have now carried out a detailed MO study of the molecules *I*–*IV* on the basis of semi-empirical and non-empirical wave functions. The published paper[5] on application of the CNDO/2 method to the pyran molecules only deals with their reduction properties and does not give any further characteristics of molecular energy and distribution. The molecule of 4*H*-pyran (*II*) was also calculated[6] by the *ab initio* MO method in the minimum STO-3G basis set presuming idealized geometry, and the orbital energies were correlated (in a set with other structurally allied compounds) with experimentally found ionisation potentials.

CALCULATIONS

All the quantum-chemical calculations were realized on a computer CYBER 172. The semi-empirical calculations of the molecules *I—IV* were carried out by the standard CNDO/2 method with standard parametrization[7], the ideal valence angles and bond lengths of plane arrangement of the heterocycles *I* and *II* being chosen beforehand as it was the case in ref.[6] for the compound *II*. The MO models *I—IV* were oriented in the coordinate system so that a maximum number of the atomic centres might lie in the *xy* plane. The calculated starting CNDO/2 models were further optimized by the gradient method with respect to all geometrical degrees of freedom[8] (800 to 2500 iterations). The molecular geometries optimized in this way (Table I) were used further as the input data for the *ab initio* calculations of energy and distribution characteristics using the standard program Gaussian-70 (Tables II to VIII). In this way we obtained the non-empirical SCF energies for the molecules *I—IV* after 12 to 20 iterations.

TABLE I

Geometry of the Molecules *I*—*IV* Optimized with Respect to All Degrees of Freedom on the Basis of CNDO/2 Wave Functions

Bond	Length pm	Valence angle	Magnitude °	Torsion angle	Magnitude °
			2*H*-pyran (*I*)		
O(1)—C(2)	138·32	O(1)—C(2)—C(3)	118·2	O(1)—C(2)—C(3)—C(4)	7·6
C(2)—C(3)	145·46	C(2)—C(3)—C(4)	121·7	C(2)—C(3)—C(4)—C(5)	0·1
C(3)—C(4)	133·69	C(3)—C(4)—C(5)	118·5	C(3)—C(4)—C(5)—C(6)	1·6
C(4)—C(5)	143·57	C(4)—C(5)—C(6)	118·0	C(4)—C(5)—C(6)—O(1)	0·0
C(5)—C(6)	133·61	C(5)—C(6)—O(1)	126·0	C(5)—C(6)—O(1)—C(2)	—0·4
C(2)—H(a)	113·10	H(a)—C(2)—O(1)	106·8	H(a)—C(2)—O(1)—C(6)	—120·0
C(2)—H(b)	113·10	H(b)—C(2)—O(1)	106·5	H(b)—C(2)—O(1)—C(6)	129·7
H(3)—C(3)	111·59	H(3)—C(3)—C(2)	115·4	H(3)—C(3)—C(2)—O(1)	176·9
H(4)—C(4)	111·68	H(4)—C(4)—C(3)	122·4	H(4)—C(4)—C(3)—C(2)	176·9
H(5)—C(5)	111·36	H(5)—C(5)—C(4)	120·8	H(5)—C(5)—C(4)—C(3)	—179·9
H(6)—C(6)	111·83	H(6)—C(6)—C(5)	125·0	H(6)—C(6)—C(5)—C(4)	—178·6
C(6)—O(1)	135·98	C(6)—O(1)—C(2)	117·5	C(6)—O(1)—C(2)—C(3)	—5·1
			4*H*-pyran (*II*)		
O(1)—C(2)	136·49	O(1)—C(2)—C(3)	127·2	O(1)—C(2)—C(3)—C(4)	9·3
C(2)—C(3)	133·17	C(2)—C(3)—C(4)	123·3	C(2)—C(3)—C(4)—C(5)	—4·6
C(3)—C(4)	145·75	C(3)—C(4)—C(5)	108·1	C(3)—C(4)—C(5)—C(6)	4·6
C(4)—C(5)	145·75	C(4)—C(5)—C(6)	123·3	C(4)—C(5)—C(6)—O(1)	0·3
C(5)—C(6)	133·17	C(5)—C(6)—O(1)	127·2	C(5)—C(6)—O(1)—C(2)	0·1
C(6)—O(1)	136·49	C(6)—O(1)—C(2)	110·4	C(6)—O(1)—C(2)—C(3)	—7·6
H(2)—C(2)	111·88	H(2)—C(2)—C(3)	123·7	H(2)—C(2)—C(3)—C(4)	—179·9
H(3)—C(3)	111·65	H(3)—C(3)—C(4)	118·2	H(3)—C(3)—C(4)—C(5)	175·3
H(a)—C(4)	112·84	H(a)—C(4)—C(5)	111·2	H(a)—C(4)—C(5)—C(6)	—117·6
H(b)—C(4)	112·84	H(b)—C(4)—C(5)	111·5	H(b)—C(4)—C(5)—C(6)	127·6
H(5)—C(5)	111·66	H(5)—C(5)—C(6)	118·5	H(5)—C(5)—C(6)—O(1)	—179·8
H(6)—C(6)	111·89	H(6)—C(6)—O(1)	109·1	H(6)—C(6)—O(1)—C(2)	—180·0
			cis-2,4-pentadienal (*III*)		
O(1)—C(2)	126·36	O(1)—(C2)—C(3)	125·6	all the atoms lie in the same plane	
C(2)—C(3)	143·15	C(2)—C(3)—C(4)	126·7		
C(3)—C(4)	133·85	C(3)—C(4)—C(5)	128·9		
C(4)—C(5)	143·68	C(4)—C(5)—C(6)	126·8		
C(5)—C(6)	132·45	H(a)—C(6)—H(b)	111·4		
H(4)—C(4)	112·11	H(4)—C(4)—C(3)	117·2		
H(5)—C(5)	111·99	H(5)—C(5)—C(4)	115·4		
H(3)—C(3)	111·84	H(3)—C(3)—C(4)	118·8		
H(2)—C(2)	112·35	H(2)—C(2)—C(3)	118·3		
H(a)—C(6)	111·26	H(a)—C(6)—C(5)	124·5		
H(b)—C(6)	111·26	H(b)—C(6)—C(5)	123·9		

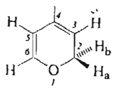
TABLE I
(*Continued*)

Bond	Length pm	Valence angle	Magnitude °	Torsion angle	Magnitude °
		trans-2,4-pentadienal (*IV*)			
O(1)—C(2)	126·38	O(1)—C(2)—C(3)	125·8	all the atoms lie in the same plane	
C(2)—C(3)	143·15	C(2)—C(3)—C(4)	125·6		
C(3)—C(4)	133·92	C(3)—C(4)—C(5)	128·1		
C(4)—C(5)	143·67	C(4)—C(5)—C(6)	126·6		
C(5)—C(6)	132·45	H(a)—C(6)—H(b)	111·4		
H(5)—C(5)	111·96	H(5)—C(5)—C(4)	115·3		
H(4)—C(4)	112·10	H(4)—C(4)—C(3)	117·8		
H(3)—C(3)	111·84	H(3)—C(3)—C(4)	119·3		
H(2)—C(2)	112·34	H(2)—C(2)—C(3)	118·1		
H(a)—C(6)	111·25	H(a)—C(6)—C(5)	124·2		
H(b)—C(6)	111·26	H(b)—C(6)—C(5)	124·3		

RESULTS AND DISCUSSION

Molecular structure. From the CNDO/2 models optimized with respect to all degrees of freedom (Table I) it can be concluded that the both pyrans *I* and *II* have not completely plane rings. Although the deviations from plane conformations of the heterocycles are not large, in the both cases there is an abvious tendency to assume the energetically more favourable chair conformations. In this context it is worth mentioning that similar deviations from plane ring arrangement are observed with the structurally similar 1,3- and 1,4-cyclohexadienes[9-13]. The heterocycle of 2*H*-pyran (*I*) exhibits the twisted boat type, the centres O(1) and C(2) showing more and less marked deviations, respectively, from the plane of the double bonds C(3)=C(4) and C(5)==C(6) which include an angle of about 1·6°. On the contrary, geometry of the 4*H*-pyran (*II*) molecule shows the regularities corresponding to the C_{2v} point group, the symmetry plane passing through the atomic centres O(1),C(4), H(a) and H(b) of the boat form of the heterocycle. The optimization procedure[8] introduces some important changes into the ideal geometry[6] of the molecule *II*: shortening of the bonds C(3)--C(4) and C(4)–C(5), diminishing of valence angle C(2)–O(1)–C(6), and non--zero torsion angles C(2)–C(3)–C(4)–C(5) and C(3)–C(2)–O(1)–C(6), respectively. Most of the calculated bond lengths and angles of the both isomers *I* and *II* show "normal" values corresponding to localization of double bonds in the sense of classical chemical formulas *I* and *II*. Only the valence angles for H(a)–C(2 or 4)–

–H(b) are somewhat lower, *i.e.* 103·5°. A more significant anomaly is obviously the high value of the valence angle O(1)–C(2)–C(3), *i.e.* 118·2° in the isomer *I*, which causes considerable deformation of tetrahedral configuration of CH_2 group, and this fact could be connected with lability of the cycle[1] in the molecule *I*. On the contrary, the valence angles in CH_2 group of the molecule of the 4*H*-isomer *II* do not show such extent of "deformation".



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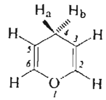

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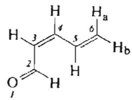

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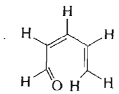
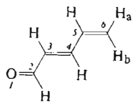


IIIa



IV

The geometrically optimized CNDO/2 models of conformers of *cis*- and *trans*-2,4-pentadienals given in the formulas *III* and *IV* are planar and do not show anomalous values of bond lengths and angles (Table I), which indicates a relatively higher stability of the corresponding molecular structures as compared with the valence isomer *I*. It is noteworthy that the gradient procedure does not lead to any energy minimum corresponding to conformation of the *cis*-isomer type *IIIa*, and,

TABLE II

Calculated Total and Relative Energies for MO Models of Compounds *I*–*IV*

Compound	$-E_{tot}$, a.u.			E_{rel}, kJ mol^{-1}		
	CNDO/2	STO-3G	4–31G	CNDO/2	STO-3G	4-31G
I	58·4916	264·2855	267·2356	7·10	19·19	5·78
II	58·4943	264·2928	267·2378	0·00	0·0	0·0
III	58·2030	264·2315	267·2414	765·57	161·10	– 9·46
IV	58·2022	264·2348	267·2459	767·67	152·43	–21·29

TABLE III

Comparison of Some Orbital Energies Calculated by Various MO Methods
All the data are given in a.u.

Order MO	2*H*-Pyran (*I*)			4*H*-Pyran (*II*)			*cis*-2,4-Pentadienal (*III*)			*trans*-2,4-Pentadienal (*IV*)		
	CNDO/2	STO-3G	4-31G	CNDO/2	STO-3G	4-31G	CNDO/2	STO-3G	4-31G	CNDO/2	STO-3G	4-21G
5′	0·281	0·615	0·286	0·277	0·607	0·284	0·259	0·603	0·261	0·261	0·612	0·271
4′	0·251	0·579	0·267	0·257	0·570	0·273	0·246	0·533	0·238	0·244	0·532	0·244
3′	0·249	0·531	0·263	0·250	0·550	0·225	0·228	0·446	0·214	0·225	0·443	0·219
2′	0·248	0·412	0·226	0·185	0·341	0·214	0·195	0·322	0·174	0·198	0·326	0·189
1′ (LUMO)	0·117	0·248	0·129	0·167	0·301	0·173	0·043	0·177	0·053	0·043	0·176	0·051
1 (HOMO)	—0·395	—0·216	—0·284	—0·415	—0·238	—0·314	—0·466	—0·267	—0·345	—0·464	—0·266	—0·344
2	—0·517	—0·377	—0·437	—0·514	—0·331	—0·382	—0·489	—0·335	—0·423	—0·497	—0·338	—0·426
3	—0·543	—0·392	—0·470	—0·547	—0·422	—0·481	—0·569	—0·389	—0·460	—0·559	—0·390	—0·460
4	—0·646	—0·439	—0·499	—0·564	—0·424	—0·502	—0·609	—0·447	—0·509	—0·606	—0·448	—0·508
5	—0·676	—0·449	—0·511	—0·673	—0·510	—0·568	—0·651	—0·460	—0·529	—0·653	—0·460	—0·528

consequently, it is possible to presume the conformer *III* to be the primary intermediate from the ring opening of the 2*H*-pyran (*I*).

Energy characteristics. Table II shows that the calculated total energies of MO models *I*–*IV* decrease according to the calculation method in the order CNDO/2 > > STO-3G > 4-31G, the differences between the E_{tot} values calculated by the both *ab initio* methods are about 3 a.u. This is quite the expected result, but the relative values of these energies E_{rel} show that the 4-31G calculations differ qualitatively from the STO-3G and CNDO/2 calculations in the statements about relative energetic stability of the pyrans *I* and *II* as compared to that of the dienals *III* and *IV*. Only if the 4-31G base is used, the open forms *III* and *IV* are preferred energetically, so that the equilibrium systems *I* ⇌ *III* and *III* ⇌ *IV* are expected to be shifted unambiguously to the right. This fact agrees with the experimental findings[1] that so far it has only been possible to prove the *cis*-dienal *III* instead of the compound *I*, the former substance undergoing obviously the isomerization into the *trans*-isomer *IV* at enhanced temperature. On the whole, however, all the calculations carried out lead to an identical result that the 4*H*-pyran molecule (*II*) represents an energetically more stable system than the 2*H*-isomer *I*.

Table III compares the energies of the frontier and the next MOs. It is interesting that the CNDO/2 orbital energies are generally closer to the values obtained by means of the split-valence base 4-31G than the analogous STO-3G data. The latter orbital

TABLE IV

Comparison of Calculated and Found Vertical Ionization Potentials of 4*H*-Pyran (*II*)

All the data are in eV, in the case of the theoretical data validity of the Koopmans theorem is anticipated.

Order	CNDO/2[a]	STO-3G[b,c]	STO-3G[a]	4-31G[a]	Experimental
1	11·29	6·33	6·46	8·53	8·38
2	13·99	9·03	9·02	10·40	10·20
3	14·88	11·01	11·47	13·08	12·00
4	15·35	11·70	11·53	13·66	12·50
5	18·31	13·57	13·87	15·77	14·00
6	18·92	14·06	14·17	15·97	14·80
7	19·87	15·08	14·49	16·06	15·30
8	20·47	15·60	15·54	17·19	16·10
9	22·60	16·11	16·25	17·68	17·70
10	25·69	16·75	16·32	18·19	

[a] The optimized geometry of the molecule; [b] the non-optimized geometry of the molecule; [c] taken from ref.[6].

energies are too low and too high for the bonding and antibonding MOs, respectively (*cf.* similar findings *e.g.* in refs[14–16]). In this connection it becomes noteworthy to what extent the energies of the bonding MOs of the compound *II* interpret its ionization potentials measured[6] by the PES method. From Table IV it is seen that the Koopmans theorem applies to the 4-31G orbital energies with satisfactory accuracy in the case of the first two ionization potentials. The authors[6] found that there exists a tight linear correlation relation between the STO-3G orbital energies and experimental ionization potentials. The numerical values in Table IV indicate that it would be possible to find analogous relations for the orbital energies calculated by us, too. If, from now on, we only take the 4-31G frontier orbital energies, then the HOMO energies of the models *I*–*IV* indicate that the pyrans *I* and *II* will be more reactive to electron-acceptors (−0·28 and −0·31 a.u., respectively). On the contrary, the LUMO energies indicate an opposite relation to electron-donors (+0·13 and +0·17 a.u. for the heterocycles *I* and *II*, respectively, compared with +0·05 a.u. for the aldehydes *III* and *IV*).

Nodal shape of the frontier orbitals. The LCAO expansions of the frontier MOs obtained for the compounds *I*–*IV* by the 4-31G calculation are given in Table V. As the optimized MO models *I* and *II* contain almost plane cyclic systems, and the models *III* and *IV* are completely plane (Table I), the exclusive particiaption of $2p_z$ and $2p_z'$ AOs for the oxygen and carbon atoms, respectively, and that of the antisymmetrical combinations of 1*s* AOs for the hydrogen atoms H(a) and H(b) can be considered as unambiguous evidence of π character of all the frontier orbitals. Analysis of nodal properties of these MOs, however, indicates at the same time that there are some typical differences in electronic structure of the heterocyclic systems *I* and *II*. In the both cases the participation of the abovementioned 1*s* AOs in the HOMO (Table V) indicates hyperconjugation of CH_2 groups with π electron system of the pyran rings. In the 2*H*-pyran (*I*) the nodal planes of the HOMO are perpendicular to the bonds O(1)–C(2), C(2)–C(3), C(4)–C(5), C(6)–O(1), C(2)–H(a) and C(2)–H(b) expressing thus antibonding interactions between the corresponding atomic centres. Hence, in this case hyperconjugation represents a destabilizing factor, and the compound *I* should exhibit a weakening or even splitting of the said bonds during thermal reactions. In the case of the O(1)–C(2) bond this fact follows from the cited experimental findings[1]. In the 4*H*-pyran (*II*) the nodal planes of the HOMO are perpendicular to the bonds O(1)–C(2), (C3)–C(4), C(4)–C(5), C(4)–H(a), C(4)–H(b) and C(6)–O(1), which should cause weakening of bonds in the CH_2 group, too. This fact agrees with the experimentally observed[4,5] tendency of the compound *II* to be aromatized to pyrylium cation. As far as the LUMO character is concerned, the model *I* exhibits nodal planes perpendicular to the bonds C(2)–C(3), C(3)–C(4), C(5)–C(6) and C(6)–O(1) with participation of hyperconjugation of the CH_2 group. Hence, electronic excitation of the compound *I* should not mar-

TABLE V

LCAO Expansions for Frontier 4-31G MOs of the Molecules *I*—*IV*

Only the members with the expansion coefficients above 0·1 are given; meaning of the symbols for AOs: $p_z = 2p_z(I)$, $p'_z = 2p_z(\text{O})$, $s = 1s(I)$, $s' = 1s(\text{O})$.

HOMO	LUMO
2*H*-pyran (*I*)	
0·2408p_zO(1) + 0·2994p'_zO(1)	0·1387p_zO(1) + 0·1966p'_zO(1)
—0·1034p_zC(2)	
0·2693p_zC(3) + 0·2846p'_zC(3)	—0·2826p_zC(3) — 0·5413p'_zC(3)
0·1940p_zC(4) + 0·2268p'_zC(4)	0·2306p_zC(4) + 0·4297p'_zC(4)
—0·2526p_zC(5) — 0·2954p'_zC(5)	0·1645p_zC(5) + 0·2915p'_zC(5)
—0·2470p_zC(6) — 0·2241p'_zC(6)	—0·3033p_zC(6) — 0·5091p'_zC(6)
—0·1148sH(a) — 0·1636s'H(a)	+ 0·1258s'H(a)
0·1079sH(b) + 0·1495s'H(b)	— 0·1305s'H(b)
4*H*-pyran (*II*)	
—0·3042p_zO(1) — 0·3177p'_zO(1)	
0·1901p_zC(2) + 0·1777p'_zC(2)	—0·2712p_zC(2) — 0·5173p'_zC(2)
0·2384p_zC(3) + 0·2758p'_zC(3)	0·2546p_zC(3) + 0·5333p'_zC(3)
—0·1204p_zC(4) — 0·1380p'_zC(4)	
0·2378p_zC(5) + 0·2745p'_zC(5)	—0·2528p_zC(5) — 0·5298p'_zC(5)
0·1896p_zC(6) + 0·1772p'_zC(6)	0·2694p_zC(6) + 0·5142p'_zC(6)
0·1327sH(a) + 0·1705s'H(a)	
—0·1236sH(b) — 0·1620s'H(b)	
***cis*-2,4-pentadienal (*III*)**	
0·2081p_zO(1) + 0·1881p'_z(O1)	0·2503p_zO(1) + 0·2990p'_zO(1)
	—0·2231p_zC(2) — 0·2684p'_zC(2)
—0·2913p_zC(3) — 0·3047p'_zC(3)	—0·1976p_zC(3) — 0·3287p'_zC(3)
—0·2049p_zC(4) — 0·2055p'_zC(4)	0·2704p_zC(4) + 0·4177p'_zC(4)
0·2091p_zC(5) + 0·2143p'_z(C5)	0·1137p_zC(5) + 0·1659p'_zC(5)
0·2651p_zC(6) + 0·2633p'_zC(6)	—0·2305p_zC(6) — 0·3687p'_zC(6)
***trans*-2,4-pentadienal (*IV*)**	
—0·2120p_zO(1) — 0·1934p'_z(O1)	0·2502p_zO(1) + 0·3018p'_zO(1)
	—0·2212p_zC(2) — 0·2780p'_zC(2)
0·2891p_zC(3) + 0·2997p'_zC(3)	—0·1936p_zC(3) — 0·3110p'_zC(3)
0·2019p_zC(4) + 0·2055p'_zC(4)	0·2676p_zC(4) + 0·3974p'_zC(4)
—0·2101p_zC(5) — 0·2170p'_zC(5)	0·1117p_zC(5) + 0·1866p'_zC(5)
—0·2666p_zC(6) — 0·2642p'_zC(6)	—0·2347p_zC(6) — 0·3836p'_z(C6)

kedly weaken the O—CH_2 bond. On the contrary, the LUMO of the model *II* exhibits two mutually perpendicular nodal planes, one between the bonds C(2)–C(3) and C(5)–C(6) and the other crossing the atomic centres O(1), C(4), H(a) and H(b). The nodal character of the frontier MOs of the dienals *III* and *IV* is slightly influenced by *cis-trans* isomerism. The HOMOs have two nodal planes perpendicular to the bonds O(1)–C(2)–C(3) and C(4)–C(5), respectively, whereas the LUMOs have three planes perpendicular to the double bonds O(1)=C(2), C(3)=C(4) and C(5)==C(6). It is noteworthy that the nodal character of the frontier MOs of the compounds *I*–*IV* calculated by the CNDO/2 and STO-3G methods is the same in all the cases, and the corresponding LCAO expansions only differ in absolute values of the expansion coefficients.

Charge distribution. Table VI gives total, σ and π electronic charges Q_{tot}, Q_{sigma}, Q_{pi} in the MO models *I*–*IV* calculated with the use of the 4-31G basis set. Distribution of the total charges shows identical qualitative features in all the cases: positive values Q_{tot} at hydrogen atoms and carbon centres of CO bonds and negative Q_{tot} values at the other carbon centres. The same is the distribution of σ charges in the dienals *III* and *IV*, whereas in the heterocycles *I* and *II* the Q_{sigma} values are always positive at oxygen atoms. The π electron charges show characteristic alternating distribution in the dienals *III* and *IV*, whereas in the pyrans *I* and *II* this alternation is disturbed by negative Q_{pi} values at the tetrahedral carbon centres C(2) and C(4) produced by hyperconjugation. Typical of the cyclic molecules *I* and *II* are the enormously high negative Q_{pi} charges at the oxygen atoms (−0·868 and −0·845, respectively) which influence strongly also the corresponding total charges Q_{tot} (−0·749 and −0·735, respectively). The easy O(1)–C(2) bond splitting in the 2*H*-isomer *I* (ref.[1]) seems to be connected with strong repulsion of negative π charges at the centres O(1) and C(2) which is not sufficiently compensated by positive σ charges at the same centres. It is typical of the dienals *III* and *IV* that the influence of *cis-trans* isomerism on all types of the investigated characteristics of charge distribution is quite negligible.

If the 4-31G charge characteristics are used as a criterion of "the best" theoretical data, then it is possible to estimate relative quality of the CNDO/2 and STO-3G charge characteristics with respect to them. Table VII compares these values on the basis of the differential charge $\Delta Q_C = Q_{tot}(4\text{-}31G) - Q_{tot}(C)$. The differences $\Delta Q_C > 0$ correspond to relative underestimation of the absolute value of negative charge calculated by the method *C* (CNDO/2 or STO-3G), and $\Delta Q_C < 0$ corresponds to similar underestimation of positive charge. Confrontation of the values Q_{tot} and Q_C in Tables VI and VII leads to a conclusion that, as far as the carbon and oxygen centres are concerned, the less perfect CNDO/2 and STO-3G calculations underestimate absolute value of charges at the individual atoms, *i.e.* they overestimate the electron delocalization between them. The situation is just opposite with the hydrogen atoms, the electron localization at these centres being most over-

TABLE VI

The Total and Partial 4-31G Charge Densities Q_i Calculated for the Models *I*—*IV*

Q_i	O(1)	C(2)	C(3)	C(4)	C(5)	C(6)	H(2)	H(3)	H(4)	H(5)	H(6)	H(a)	H(b)
						2*H*-pyran (*I*)							
total	—0·749	0·045	—0·235	—0·158	—0·293	0·238	—	0·194	0·199	0·203	0·215	0·168	0·173
sigma	0·119	0·167	—0·203	—0·170	—0·159	0·175							
pi	—0·868	—0·122	—0·032	0·012	—0·134	0·063							
						4*H*-pyran (*II*)							
total	—0·735	0·190	—0·230	—0·337	—0·230	0·190	0·212	0·191	—	0·191	0·212	0·174	0·172
sigma	0·110	0·190	—0·155	—0·232	—0·155	0·190							
pi	—0·845	0·000	—0·075	—0·105	—0·075	0·000							
						cis-2,4-pentadienal (*III*)							
total	—0·576	0·330	—0·277	—0·132	—0·183	—0·325	0·172	0·222	0·207	0·195	—	0·179	0·177
sigma	—0·234	0·067	—0·212	—0·246	—0·164	—0·375							
pi	—0·342	0·262	—0·065	0·114	—0·018	0·050							
						trans-2,4-pentadienal (*IV*)							
total	—0·579	0·332	—0·270	—0·131	—0·175	—0·328	0·171	0·217	0·198	0·199	—	0·188	0·188
sigma	—0·231	0·069	—0·210	—0·242	—0·163	—0·374							
pi	—0·348	0·263	—0·060	0·111	—0·012	0·046							

TABLE VII

Comparison of Total Charge Distribution in the MO Models *I*—*IV* Obtained by CNDO/2, STO-3G and 4-31G Calculations
The values used for the comparison are $\Delta Q = Q_{tot}(4\text{-}31G) - Q_{tot}(\text{CNDO/2 or STO-3G})$.

Calculation	O(1)	C(2)	C(3)	C(4)	C(5)	C(6)	H(2)	H(3)	H(4)	(H5)	H(6)	H(a)[a]	H(b)[a]
						2*H*-pyran (*I*)							
CNDO/2	0·55	0·14	0·19	0·20	0·22	—0·07	—	—0·19	—0·21	—0·21	—0·20	—0·21	—0·21
STO-3G	0·60	—0·02	0·16	0·11	0·17	—0·15	—	—0·13	—0·14	—0·14	—0·14	—0·12	—0·12
						4*H*-pyran (*II*)							
CNDO/2	0·56	—0·04	0·17	0·27	0·17	—0·04	—0·23	—0·19	—	—0·19	—0·23	—0·19	—0·19
STO-3G	0·51	—0·12	0·14	0·24	0·14	—0·12	—0·14	—0·13	—	—0·13	—0·14	—0·12	0·12
						cis-2,4-pentadienal (*III*)							
CNDO/2	0·34	—0·10	0·23	0·19	0·19	0·32	—0·21	—0·21	—0·21	—0·19	—	—0·17	0·18
STO-3G	0·38	—0·22	0·20	0·10	0·12	0·23	—0·13	—0·15	—0·14	—0·13	—	—0·12	—0·12
						trans-2,4-pentadienal (*IV*)							
CNDO/2	0·34	—0·10	0·22	0·19	0·18	0·32	—0·21	—0·20	—0·20	—0·20	—	—0·17	—0·18
STO-3G	0·38	—0·22	0·19	0·10	0·11	0·23	—0·13	—0·15	—0·14	—0·14	—	—0·12	—0·12

[a] For tetrahedral atomic centres.

estimated just by the CNDO/2 method in agreement with the common experience[17]. This antagonistic expression of localization of electrons at hydrogen and other atomic centres is characteristically manifested in the values of electric dipole moments of the compounds *I*–*IV* calculated by the methods CNDO/2, STO-3G and 4-31G. It is obvious (Table VIII) that the CNDO/2 values lie between the "better" 4-31G and the "worse" STO-3G dipole moments in accordance with the unsuitability of the latter simple version of the *ab initio* methods for calculation of global characteristics of electron distribution, which has been already observed in a number of further MO models of organic molecules[18–20].

CONCLUSIONS

The 4-31G calculations carried out show that high lability of 2*H*-pyran molecules (*I*) under usual laboratory conditions is obviously due to its higher molecular energy as compared with the non-cyclic valence isomer *III*. This energy difference is expressed by the 4-31G energies (Table II) only partially, and it will be probably higher after involving the correlation energy, which could not yet be realized for technical reasons. Considerable lability of some bonds in the molecule I is further supported by the nodal properties of the HOMO and by deformations of valence angles in CH_2 group. The relatively higher stability of the molecules of 4*H*-pyran (*II*) agrees with the generally lower CNDO/2, STO-3G and 4-31G molecular energies as compared with those of the isomer *I*, with the non-deformed geometry of the CH_2 group and, according to the HOMO and the LUMO energies, with a relatively lower tendency to donor-acceptor interactions.

The results obtained for the MO models *I*–*IV* show that the *ab initio* calculations in the minimum STO-3G basis set do not give any markedly better results than the simple-empirical CNDO/2 method does, especially so in the case of orbital energies and electron distribution characteristics.

TABLE VIII

Calculated Electrical Dipole Moments of the Compounds *I*—*IV*

All the data in Cm . 10^{-30}.

Molecule	CNDO/2	STO-3G	4-31G
I	4·229	2·565	4·722
II	3·382	2·455	5·146
III	11·406	8·578	17·255
IV	11·576	8·708	17·502

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