Quantum-chemical study of manifestations of conjugation in molecules containing conjugated C=C and C=O bonds

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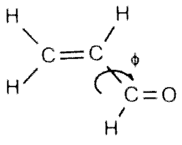
Based on the MNDO calculations of the electronic structure of the molecules of acrolein, glyoxal, and butadiene, possible mechanisms of the conjugation in systems containing conjugated C=C and C=O bonds have been analyzed. In the electronic ground state of *s-trans*-acrolein, the π,π-conjugation is very small, whereas in the first excited electronic state, the conjugation is substantial. In the ground state of *s-trans*-glyoxal, the π,π-conjugation should manifest itself clearly but should be weaker than in butadiene, whereas in the first excited electronic state, this conjugation should be more pronounced. Alternation of double and single bonds in the classic structural formula of a molecule does not ensure that this molecule exhibits the properties of a π-conjugated system even in planar conformations.

Key words: unsaturated carbonyl compounds, MNDO method, conformations, electronic spectra, π,π- and σ,π-conjugation.

Modern *ab initio* quantum-chemical methods, which use the Hartree—Fock approximation with extended basis sets and adequately take into account the electron correlation, make it possible to calculate the characteristics of medium-sized molecules with a rather high degree of accuracy. However, it is generally difficult to interpret the results of these calculations within the framework of a particular simple model, whereas it is just this interpretation of theoretical and experimental results that is ultimately of chemical interest.

In theoretical organic chemistry, particular fragments (atomic groups) are generally chosen in the structures of complex molecules because some properties appear to be approximately additive. However, the deviations from additivity are rather substantial, for example, in systems containing alternating double and single CC bonds. Studies of these molecules gave rise to the concept of conjugation based on the representation that delocalized MOs are formed from localized occupied and unoccupied fragment orbitals (FOs). The possibility and the energy effect of the mixing of the fragment orbitals are determined by their similarity in energy and by their overlap. However, calculations of particular systems remain necessary from the standpoint of interpretation of experimental results in terms of the structural approaches commonly used in organic chemistry as well as for a clearer understanding of the nature of the factors determining the characteristic features of the electronic structures of complex molecules within the framework of these approaches. This understanding is essential, in particular, in order to choose the systems, in which the migration of the electron density and the excitation energy are possible; these aspects are important in searching for new types of elements for molecular electronics, in analyzing mechanisms of biological activities, and in solving many other problems.

This work is devoted to studies of the mechanism and possible manifestations of the conjugation of C=C and C=O double bonds using the acrolein (**1**) molecule as an example in comparison with the molecules of butadiene and glyoxal. All calculations were carried out by the conventional MNDO method[1] using the AMPAC program (Version 1.0).



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Quantum-chemical calculations of molecule **1** have been carried out many times (see, for example, Refs. 1—7); however, these studies have been devoted primarily to obtaining data that coincide with the characteristics determined experimentally (the geometry, the barrier to rotation about a single C—C bond, photoelectron spectra, *etc.*) with the maximum possible accuracy. To our knowledge, a detailed analysis of the electronic structure of acrolein based on the concept of the conjugation of the C=C and C=O bonds has not been carried out.

We calculated the *s-trans*, *gauche*, and *s-cis* conformers of acrolein (ϕ = 180°, 90°, or 0°). Of the two planar conformers, we considered one conformer (ϕ = 180°) in detail, because it is experimentally known[8] that ~ 95 % of acrolein occurs at room temperature in this form. Calculations of the *gauche* conformer are of interest for comparison, because in this case π,π-conjugation should be virtually absent. In calculations of all conformers, we used the values of the bond angles and

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bond lengths of molecule **1** reported in Ref. 9 for the gaseous phase. These parameters were not optimized; optimization rather weakly affects the molecular characteristics discussed below and, hence, is insignificant in the qualitative consideration.

The energies of the conformers of molecule **1** obtained in this work do not entirely agree with the known experimental data and the results obtained by *ab initio* methods. Thus, it has been demonstrated[4,7] by *ab initio* calculations with the 6-31G*, 6-31G,** and 6-311G** basis sets that the *s-trans* conformation is optimum for **1**, and the *s-cis* and *gauche* conformers are less favorable by ~2 and ~ 7 kcal/mol (the barrier), respectively. These results agree with the experimental data:[10] ~1.5 and ~8 kcal/mol.

According to the results of our MNDO calculations, the energies of the above-mentioned conformers differ by ≤ 1 kcal/mol; as expected, the most favorable conformer is the *s-trans* conformer, but when the *s-trans* → *gauche* → *s-cis* transitions occur, the energy increases monotonically, *i.e.*, no local extrema were found. Calculations with optimization of all bond lengths and bond angles gave analogous results. The alternative semiempirical methods (MINDO/3 and AM1[7]) gave the same results, whereas the *ab initio* calculations with the STO-3G and 3-21G basis sets (although they are indicative of the presence of a barrier corresponding to the *gauche* conformation) underestimate substantially the differences in the energies of the conformers.[11]

Therefore, our calculations do not allow us to establish the preferred conformation of acrolein with certainty. The suggestion that this conformation is determined principally by steric factors and by a slight charge redistribution that occurs during conformational transitions (the basis set involving the polarization functions is required to account for redistribution) rather than by conjugation (see Refs. 4, 7, and 11) is, evidently, reasonable. Since the MNDO method gives a qualitatively adequate description of the structure and positions of different types of MO levels on the energy scale[12] as well as of the character of the change in the energy of the electron transitions in the series of related compounds,[13] we believe that, in spite of the particular limitations of the MNDO method, the analysis of the electronic structure of molecule **1** discussed below makes it possible to interpret certain characteristic features of compounds with conjugated C=C and C=O bonds based on rather simple model representations.

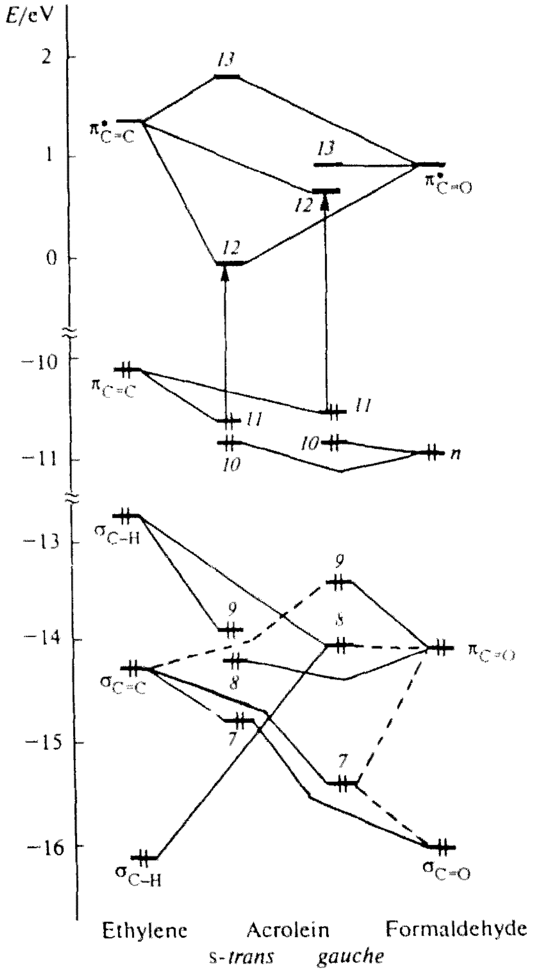

Fig. 1. Scheme of the energy levels of the frontier MOs of acrolein and of the $CH_2=CH_2$ and $H_2C=O$ molecule-quasi-fragments. Electron transitions are indicated by vertical arrows.

Figure 1 shows the positions of the levels of the frontier MOs of *s-trans*- and *gauche*-acrolein, ethylene, and formaldehyde on the energy scale. Ethylene and formaldehyde are used as models for the fragments (molecules-quasi-fragments) of acrolein. The solid lines indicate the principal genetic relations between the orbitals; the dashed lines indicate relations of lesser significance. Calculations of the molecules-quasi-fragments were carried out using geometries identical to those of the corresponding fragments in molecule **1**. The contributions of the fragment orbitals to the MOs were qualitatively estimated from the coefficients of the corresponding AOs in the MOs and FOs. Modeling the fragments using radicals (in this case using $CH_2=^{\cdot}CH$ and $HC^{\cdot}=O$) should allow a quantitative estimation of the above-mentioned contributions by projecting the MOs on the set of the fragment orbitals. However, our experience in calculations demonstrated that this approach leads to qualitatively identical results.*

As Fig. 1 shows, the two highest occupied MOs in the *s-trans* and *gauche* conformers of molecule **1** are localized substantially at the fragments: the HOMO are the π FO of the ethylene subsystem with a very small admixture of the $\pi_{C=O}$ and $\pi^*_{C=O}$ FOs, while the next lower-lying MO corresponds approximately to the lone

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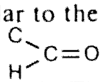
* The way of dividing a complex molecule into fragments is determined by the character of the problem and may be rather difficult. One of the possible approaches is developed in Ref. 14.

electron pair of the oxygen atom and ~65 % of this MO is localized at this atom. The 2p-AO of the oxygen atom located perpendicular to the direction of the C=O bond in the plane of the  $\overset{C}{\underset{H}{}}{>}C{=}O$ fragment makes the major contribution to this MO. The contribution of the analogous 2p-AO of the C atom of the carbonyl group is small (~4 %). Therefore, the n,$\pi_{C=C}$-overlap and the mixing are small even in nonplanar conformers (in planar conformations, these contributions are, apparently, equal to zero), in which they could be substantial if the population of the appropriate AO of the carbonyl carbon atom were higher. Mixing of π-orbitals of the C=C and C=O fragments in the planar conformers is virtually absent because of the large (~4.5 eV) difference in the energy.

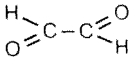
In the *gauche* conformer of molecule **1**, mixing of the substantially lower lying $\sigma_{C=C}$ and $\pi_{C=O}$ FOs is substantial. Figure 1 shows that in the planar conformer, MO *7* is the $\sigma_{C=C}$ FO with a substantial admixture of the $\sigma_{C=O}$ FO, whereas in the nonplanar conformation, an admixture of ≤10% of $\pi_{C=O}$ FO is present in MO *7*, which results in a decrease in the energy of MO *7* by ~0.7 eV. MO *8* of the planar conformer is virtually the $\pi_{C=O}$ FO, whereas in the nonplanar conformer, MO *8* contains an admixture of the $\sigma_{C=C}$ FO (~10%), and its energy is ~0.7 eV higher. Note that in the *gauche* conformer the order of the MOs is different from that in the planar conformer (see the data for MO *8* and MO *9*).

Based on the above-mentioned data and on the results of our calculations of acetaldehyde it may be concluded that the energy effects of the mixing of the $\sigma_{C=C}$,$\pi_{C=O}$ FOs in *gauche*-**1** and the *pseudo*-π_{CH_3},$\pi_{C=O}$ FOs in acetaldehyde are approximately equal: in going from formaldehyde to *gauche*-**1** as well as to acetaldehyde, the energy of the $\pi_{C=O}$ orbital increases by ~0.7 eV, but in *s-trans*-**1**, this energy slightly decreases (see Fig. 1).

It was also found that the structure and the energies of the two lowest unoccupied orbitals of molecule **1** depend substantially on the conformation. In the *gauche* conformer, these orbitals are localized at the fragments: the LUMO (MO *12*) is the virtually unchanged $\pi^*_{C=C}$ FO, and MO *13* is the $\pi^*_{C=O}$ orbital. In the planar conformer, these orbitals are substantially mixed to form two completely delocalized π^*-MOs, and their levels move far apart on the energy scale (see Fig. 1).

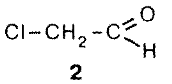
Therefore, in the planar conformer of molecule **1**, π,π-conjugation occurs for the lowest unoccupied MOs and is virtually absent for the occupied orbitals. It can be said that for molecule **1**, conjugation is negligible in the electronic ground state, whereas conjugation in the lowest excited electronic states is significant. In the *gauche* conformer, σ,π-conjugation caused by the mixing of the lower-lying $\pi_{C=O}$ and $\sigma_{C=C}$ FOs would be expected to manifest itself. Based on the conformation dependence of the energies of the frontier MOs of compound **1**, which we discussed above, it can be assumed that the first two ionization potentials will not change substantially upon the conformational transition *s-trans* → *gauche*, while the electron affinity should essentially decrease. The MNDO calculations taking into account the configuration interactions for excited singlet states (16 singly excited configurations corresponding to electron transfer from each of the four highest occupied MOs to each of four lowest unoccupied orbitals) demonstrated that the intense long-wave electron transition should be the $\pi_{C=C}\to\pi^*_{C=C-C=O}$ and $\pi_{C=C}\to\pi^*_{C=C}$ transitions in the planar and nonplanar conformers, respectively (arrows in Fig. 1), and the latter transition should shift to the higher energy region by 0.2—0.3 eV.

Let us compare the results obtained for acrolein with the results of our calculations for isostructural molecules with identical double bonds, namely, for butadiene and glyoxal. It is known that significant manifestations of π,π-conjugation are typical of butadiene. In the planar conformer, the two highest occupied and two lowest unoccupied MOs are delocalized π-orbitals that differ substantially in energy: $E_{HOMO} - E_{HOMO-1} \approx 1.4$ eV and $E_{LUMO+1} - E_{LUMO} \approx 1.6$ eV. In the *gauche* conformer, these differences are virtually equal to zero; however, the corresponding MOs remain delocalized. Because the energies of the π-fragment orbitals are equal, even very weak interaction of these orbitals (the overlap is very small) leads (in the absence of symmetry elements) to complete mixing. Therefore, in butadiene, the electron affinity as well as the first two ionization potentials should depend on the conformation; the conformation dependence of the energy of the long-wave electron transition should be more pronounced than in molecule **1**.

In glyoxal,  $\overset{H}{\underset{O}{}}{>}C{-}C{<}\overset{O}{\underset{H}{}}$, the character of the mixing of the π FOs in the *s-trans* and *gauche* conformers is qualitatively identical to that in butadiene considered above. In the planar conformer of glyoxal, the splitting of the occupied π-MOs is substantially smaller, while the splitting of the unoccupied orbitals (LUMO and LUMO + 1) is slightly larger than the corresponding values in butadiene. This is, apparently, associated with the fact that the π-electron density at the C atom for the occupied $\pi_{C=O}$ FO is substantially smaller than that at the O atom owing to the fact that the electronegativity of the oxygen atom is higher than that of the carbon atom. The opposite situation occurs for the unoccupied $\pi^*_{C=O}$ FO. Therefore, in the glyoxal molecule, the overlap of the occupied π FOs is substantially smaller, whereas the overlap of the unoccupied orbitals is higher than those in the butadiene molecule. Because the two highest occupied MOs of glyoxal correspond to the lone electron pairs of the oxygen atom, which are noticeably delocalized only at the nearest neighboring carbon atoms, the spectral manifestations of conjugation in this case would be expected to be similar to those typical of acrolein rather than of butadiene: the electron affinity rather than the two first ionization potentials should depend on the conformation.

The characteristic features of the delocalization of the unoccupied and occupied π-MOs in the planar conformers of **1** and butadiene manifest themselves also in chemical reactivity. It is well known that both electrophilic and nucleophilic 1,4-addition are typical of butadiene, and is determined by delocalization of the occupied and unoccupied π-MOs. In molecule **1**, the occupied π-MOs in the planar conformers are localized to a large degree at the fragments, whereas the unoccupied orbitals are completely delocalized. Correspondingly, electrophilic addition to **1** proceeds at isolated double bonds, while nucleophilic addition proceeds by the mechanism of 1,4-addition followed by rearrangement to the 1,2-products.[15,16] The π-MOs of cyclohexanediones that occur in the keto-enol form have an analogous structure. The particular characteristic features of nucleophilic addition of H_2O_2 to these compounds have been explained on this basis.[17]

The differences in the charges Δq on the C and O atoms of the carbonyl group in acrolein and formaldehyde, which we calculated by the MNDO method, are given in Table 1. In this table, the analogous values for molecules **2** and **3**, which were also calculated by the MNDO method,[18] are given for comparison.


$\mathrm{Cl{-}CH_2{-}C}\overset{\mathrm{O}}{\underset{\mathrm{H}}{\lessgtr}}$

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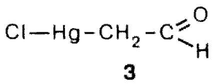
$\mathrm{Cl{-}Hg{-}CH_2{-}C}\overset{\mathrm{O}}{\underset{\mathrm{H}}{\lessgtr}}$

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It can be seen that in the *s-trans* conformer of **1**, the total charges on the atoms considered are virtually identical to those in formaldehyde, whereas in the *gauche* conformer, the C=O fragment loses ~0.02 ē. The components of the total charges in *s-trans*-**1** are as follows: $\Delta q^{C}_{\pi} = -0.030$, $\Delta q^{O}_{\pi} = -0.005$, $\Delta q^{C}_{\sigma} = 0.031$, and $\Delta q^{O}_{\sigma} = 0.005$.

In the planar conformer of molecule **2**, the carbonyl group acquires ~0.01 ē and is substantially polarized; on the other hand, in *gauche*-**2**, the carbonyl group loses ~0.005 ē, and its polarization is slightly higher than in *s-trans*-**2**. In the *s-trans* conformer of molecule **3**, there is virtually no transfer of electron density to the C=O group, and only polarization is observed. This polarization is substantially smaller than that in *s-trans*-**2**, whereas in *gauche*-**3** it is even smaller but the transfer of ~0.01 ē to the C=O fragment occurs.

Table 1. Differences in charges (a.u.) on the atoms of the carbonyl group in compounds **1**, **2**, and **3** and in formaldehyde.

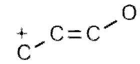
Compound	Conformation	Δq	
		C	O
1	*s-trans*	0.001	0.000
	gauche	0.012	0.006
2	*s-trans*	−0.036	0.026
	gauche	−0.037	0.042
3	*s-trans*	−0.010	0.011
	gauche	−0.009	0.000

It is believed that the above-mentioned relationships between the conformation and the degree of polarization of the C=O group are determined mainly by the difference in the mutual arrangement of the interacting polar fragments in the *s-trans* and *gauche* conformers, for example of C—Cl and C=O in molecule **2** (a field effect).

Mixing of the $\pi_{C=O}$ and pseudo-π_{CH_2} FOs is possible in the planar conformer of molecule **2**, while mixing of the $\pi_{C=O}$ and σ_{C-Cl} FOs is possible in the nonplanar conformer. Based on the results of our calculations, these fragment orbitals are rather close in energy.

It is evident from Table 1 that although the total charges on the atoms of the carbonyl group of the planar conformer of **1** are virtually identical to those in formaldehyde, a substantial shift of the π-electron density to the C=O fragment, and a shift of σ-electrons in the opposite direction, should occur. This is consistent with the results of other calculations (see, for example, Refs. 5 and 19). However, it has been suggested[19] that the shift of the π-electron density from the ethylene fragment to the carbonyl group is caused by the fact that the $\pi_{C=O}$ MO of formaldehyde lies ~4 eV lower than the $\pi_{C=C}$ MO of ethylene (because the energies of the $\pi^{*}_{C=O}$ and $\pi^{*}_{C=C}$ MOs differ only by ~0.4 eV, the mixing of the $\pi_{C=C}$ and $\pi^{*}_{C=O}$ FOs should be substantially larger than that of the $\pi_{C=O}$ and $\pi^{*}_{C=C}$ FOs). The shift of the σ-electron density in the opposite direction is attributable to the fact that in this case electron-electron repulsion decreases. Therefore, in Ref. 19 the formation of delocalized π-MOs with a noticeable contribution from unoccupied π* FOs was considered to be the origin of the change in the electron distribution. However, as is evident from Table 1 and the results discussed above, the shift of the total electron density from the C=O group in *gauche* acrolein (compared to formaldehyde), in which interfragment mixing of the π FOs is virtually absent, is of the same order as the σ-electron density transfer in *s-trans*-**1**. Based on this fact, there is good reason to suggest that the decrease in the σ-electron density at the carbonyl group in going from formaldehyde to *s-trans*-**1** is caused by the replacement of the H atom by a $CH_2{=}CH$ group because the carbon atom is a better electron acceptor than H. The shift of the π-electron density in the opposite direction is energetically favorable, because in this case the electron-electron repulsion decreases. To put it differently, in this case, the character of the redistribution of both the σ- and the π-electron density is determined by a newly formed σ-bond (C—C instead of C—H).

The results discussed clearly demonstrate that the presence of the strutural motif (two double bonds separated by a single bond) in the classic formula does not ensure that the molecule exhibits the properties of a π-conjugated system even in planar conformations. Similarity of the π FOs in energy and in the π-electron density distribution at these orbitals, which favors their overlap, is additionally required. This fact is well known; however, when structural approaches commonly accepted in organic chemistry are used, the two last-mentioned conditions are often ignored, while exceptional significance is attached to the first condition.

In Refs. 2–6, *ab initio* calculations (MP2/6-31G* and MP3/6-311++G**) of the energies of the conformations, the bond lengths, and electron density distribution for a series of $CH_2=CH-X$ molecules, in particular, for acrolein, were carried out. With the aim of providing a clear explanation for the results, it was attempted to interpret these results in terms of resonance theory and to discuss the role (the weighting factor) of the zwitterionic resonance structure  $\overset{+}{C}-C=C-O^-$. Calculations by the valence-bond method were not carried out but it was assumed that the contribution of this structure was substantial because of the presence of the conjugated C=C and C=O double bonds in molecule **1**. The authors concluded that the resonance zwitterionic structure may be of importance for acrolein in considering its reactivity and, apparently, aspects of the formation of the barrier to rotation, but this structure has no effect on the charge distribution or on the length of the single C—C bonds.

Actually, a substantial contribution of this structure would imply substantial electron transfer from C=C to C=O and shortening of the C—C bond in going from *gauche*-**1** to *s-trans*-**1**, whereas according to the results of calculations,[2–6] the electron population of the C=C fragment changes only slightly, and the C—C bond length remains virtually unchanged. Hence, it was concluded that because the resonance in molecule **1** has an unusual effect on the properties considered, this resonance calls for further investigation. However, our data, which indicate that occupied orbitals are essentially localized and unoccupied π-MOs are completely delocalized in *s-trans*-**1**, do not contradict to the results of previous calculations.[2–6]

Therefore, for the planar conformation of acrolein, noticeable π,π-conjugation is not expected in the electronic ground state, while in the first excited electronic state this conjugation should be pronounced. In *s-trans* glyoxal, π,π-conjugation in the ground state should be somewhat weaker than in butadiene, whereas in the first excited electronic state, this conjugation should be markedly stronger. This difference is associated with the fact that the overlap of the occupied π FOs of the C=O groups is slightly smaller than that of the unoccupied orbitals. Using the considered molecules as an example, it was demonstrated that it is inadequate to use only the structural approach to the problems of conjugation.

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