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The nature of the rotational barriers in simple carbonyl compounds

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Abstract—The rotational barriers around the CO and CC bonds are investigated in formic acid, ethanedial and glycolaldedyde molecules on the basis of DFT-B3LYP/aug-cc-pVDZ calculations. Natural bond orbitals analysis is applied to enhance physical understanding of rotational barriers. In the case of attractive barriers in formic acid and Gc-glycolaldehyde, the barrier originates from the loss of hyperconjugation that determines the equilibrium structures while for the repulsive barriers in ethanedial and Go-glycolaldehyde, both Lewis and hyperconjugation terms contribute.

1. Introduction

Knowledge of the energy barriers which separate conformers is important for the interpretation of several physical and chemical molecular properties. Experimentally, the potential barrier heights and torsional shape information are accessible from high-resolution FTIR spectroscopy or, for bigger molecules, from the measurement of the NMR spectra, in particular from the spin–spin coupling constants (information on torsional angles). A key problem in the interpretation of the spin–spin coupling constants is the coupling constant-structure correlation. A complementary approach to obtain information on molecular structure and energetics is offered by ab initio calculations. Although the accuracy of the ab initio calculations is still below the state-of-the-art accuracy of the spectroscopic data for molecules of chemical interest, the calculations provide information on the shape of the potential energy surfaces without any initial assumptions.

Glycolaldehyde could be regarded as a prototype for carbohydrates. It has two internal rotational degrees of freedom: the rotation of the hydroxyl group around the C–O bond and the rotation of the –CH$_2$ OH group around the C–C bond, which is attached to the carbonyl group. The rotation about CO or CC bonds adjacent to carbonyl groups is of importance in studying the properties of carbohydrates, lactames and ketones. In particular, the rotation barriers, obtained experimentally, or calculated ab initio, are being

used to parametrized potentials utilized for modeling the structures of carbohydrates, their derivatives and complexes, via molecular mechanics. The set of molecules chosen for our study is: formic acid, ethanedial and glycolaldehyde. They can be treated as derivatives of formaldehyde where hydrogen atoms have been substituted by –OH, –CHO and –CH$_2$ OH groups, respectively. For glycolaldehyde, we decided to focus on the rotation around the C–C bond.

The origin of the barrier to rotation has been the subject of many papers.[1,2] According to the electrostatic model,[1] the final value of the energy barrier which separates two conformers is determined by variation of the attractive ($A=V_{ne}$) and the repulsive ($R=T+V_{ee}+V_{nn}$) contributions to the total molecular energy during intramolecular rotation. This lead to the concept of attractive and repulsive rotation barriers.

Very recently, the paper was presented by Pophristic and Goodman on the use of delocalized natural bond orbitals (NBO) model to understand the nature of the barrier to rotation in ethane.[3] The authors used the expansion in terms of Lewis and non-Lewis-type NBO interactions, which identifies distinct physical contributions of 'steric' versus 'hyperconjugation' origin. It was found that, it is hyperconjugation that determines the equilibrium structure of ethane. This is contrary to the textbook explanation that steric repulsion between bonds, due to the overlap of the occupied bond orbitals is the origin of the barrier to rotation in ethane.[4]

In this paper, we present the results of the calculations of rotational barriers about CO and CC bonds adjacent to

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carbonyl groups in three molecules: formic acid, ethanedial and glycolaldehyde. We analyze the nature of the barrier to rotation on the basis of natural bond orbital methods NBO on the one hand and attractive and repulsive contributions on the other. The method employed is described in Section 2 of this paper. Section 3 presents the results and the summary is presented in Section 4.

2. Methods of calculations

First, let us describe briefly the meaning of the most important terms used in this study. The total energy can be represented as the sum of the kinetic energy T, the electron repulsion V_{ee}, the nuclear repulsion V_{nn} and the attractive nuclear-electron energy V_{ne} terms. The energy difference between the conformers is thus

$$\Delta E = \Delta T + \Delta V_{nn} + \Delta V_{ne} + \Delta V_{ee} \qquad (1)$$

The electron repulsion term V_{ee} can be divided into the classic Coulomb repulsion denoted as $1/2\Delta\langle PJ(P)\rangle$, the exchange term ΔE_{ex} and the correlation term ΔE_c. The exchange repulsion involves the Pauli exclusion principle which requires same-spin electrons not to occupy the same spatial region. These three terms are calculated separately[5] at the DFT level of theory and are reported as such in the Gaussian98 package.[6]

$$\Delta V_{ee} = 1/2\Delta\langle PJ(P)\rangle + \Delta E_{ex} + \Delta E_c \qquad (2)$$

The NBO model transforms a given wavefunctions into the localized form, corresponding to the one-centre (lone pair) and two-centre (bond) elements of the traditional Lewis structure.[7,8] The set of high-occupancy NBOs is supposed to represent the 'natural Lewis structure' of the molecule.

Hyperconjugation, the concept describing electron delocalization, involves electron transfer from an occupied (bonding) to an unoccupied (antibonding) orbital, leading to de-localization of the charge. The effect of the hyperconjugation is obtained by comparison with the results obtained after deletion of selected antibonding orbitals in the NBO description of the molecule. We have used the NOSTAR (NBO 4.0) option for deletion of all non-Lewis orbitals in order to obtain the energy of the idealized natural Lewis structure.[6] In our discussion, complementary to that resulting from Eq. 1, we can picture the barrier to rotation as having a 'Lewis' (localized, covalent) and 'non-Lewis' (delocalized, non-covalent, hyperconjugative) contributions to the energy of the molecule, according to the Eq. 3

$$\Delta E = \Delta E_{Lew} + \Delta E_{del} \qquad (3)$$

The non-Lewis contributions are usually much less than 1% of the covalent term.

The calculations of the energy as a function of the HCCH or HCOH dihedral angles at the B3LYP level[9] and NBO analysis have been performed using the Gaussian98 package.[6] DFT–B3LYP is a cheap and increasingly popular method for calculations of the molecular electronic structure[10] and should perform adequately for the barriers to rotation. Moreover, it allowed us to obtain separately several different terms, mentioned above. The basis set employed is aug-cc-pVDZ[11,12] containing diffuse functions required for the proper description of the outer part of the electron density.

Full geometry optimization have been performed for all the structures. To examine the effect of relaxation of internal molecular modes, we calculated the minimum-energy

Table 1. The selected geometric parameters (in Å, °) for the optimal structures of formic acid, ethanedial, Gc-and Go-glycolaldehyde calculated at B3LYP/aug-cc-pVDZ level

|	Formic acid	Ethanodial	Gc-glycolaldehyde	Go-glycolaldehyde
$r(C1–C2)$	–	1.5267	1.5186	1.5114
$r(O1–C1)$	1.2049	1.209	1.2237	1.2271
$r(H1–C1)$	1.1034	1.1134	1.1146	1.1127
$r(C2–O2)$	–	1.209	1.4307	1.4130
$r(C1–O2)$	1.3494	–	–	–
$r(H2–C2)$	–	1.1134	1.1045	1.1078
$r(H3–C2)$	–	–	1.1048	1.1064
$r(H4–O2)$	0.9732	–	0.9658	0.9742
$\alpha(O1–C1–C2)$	–	121.4	122.8	121.8
$\alpha(O1–C1–O2)$	125.0	–	–	–
$\alpha(H1–C1–C2)$	–	115.2	115.1	116.8
$\alpha(H1–C1–O2)$	109.83	–	–	–
$\alpha(C1–C2–O2)$	–	121.4	107.1	112.0
$\alpha(H2–C2–C1)$	–	115.1	108.3	107.6
$\alpha(H3–C2–C1)$	–	–	108.2	108.2
$\alpha(H4–O2–C2)$	–	–	108.5	105.6
$\alpha(H4–O2–C1)$	107.5	–	–	–
$\tau(H1–C1–C2–H2)$	–	180.0	−55.6	120.0
$\tau(H1–C1–O2–H4)$	180.0	–	–	–
$\tau(H1–C1–C2–H3)$	–	–	60.0	−122.5
$\tau(H1–C1–C2–O2)$	–	0.0	−178.0	−1.2
$\tau(O1–C1–C2–O2)$	–	180.0	1.8	178.9
$\tau(O1–C1–O2–H4)$	0.0	–	–	–
$\tau(O1–C1–C2–H2)$	–	180.0	–	–
$\tau(C1–C2–O2–H4)$	–	–	−2.1	179.8
$\tau(H2–C2–O2–H4)$	–	–	−123.0	61.2
$\tau(H3–C2–O2–H4)$	–	–	118.1	−61.4
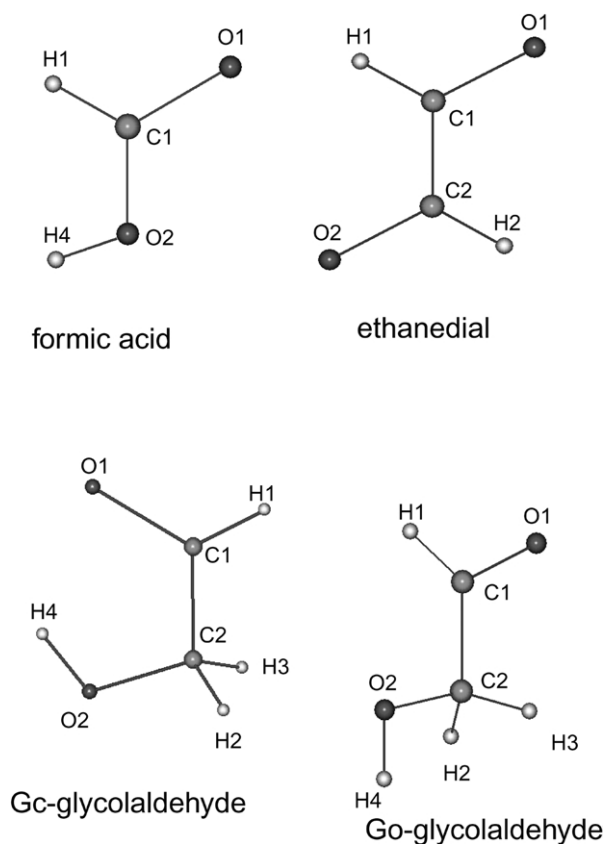
Figure 1. The structures and atom numerations in the systems under study.

paths connecting the structures. The selected geometric parameters of the optimized global minimum structures are presented in Table 1, while the structures themselves are shown in Figure 1.

3. Results and discussion

3.1. Formic acid

Free rotation in formic acid was investigated previously in many papers.[13–15] The molecule can exist in the lowest energy conformer *trans* and in the *cis* conformer of higher energy. We investigated the rotation about the CO bond changing the dihedral angle $\tau=$H4–O2–C1–H1 (see Figure 1 for atom numeration). Table 2 presents the total energy for the conformers *trans* ($\tau=180°$), *cis* ($\tau=0°$), and for the transition state at the top of the barrier ($\tau=90°$). A number

of explanations have been proposed for these energy differences.[1,13] The barrier in formic acid is said to be attractive, since the decrease of the A term is faster than the increase of the R term, $|\Delta A|>|\Delta R|$.[1] Our data confirm this statement. Various components of the energy and their changes as the molecule is rotated are displayed in Table 2. The variations of the terms V_{nn}, V_{ne} and V_{ee} during conformational changes are depicted in Figure 2a.
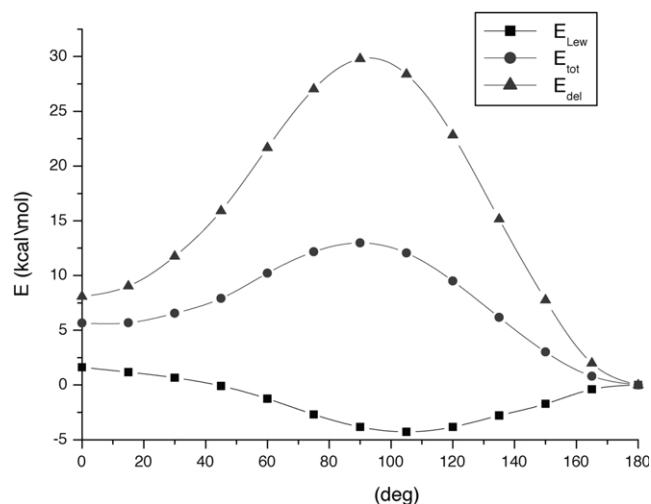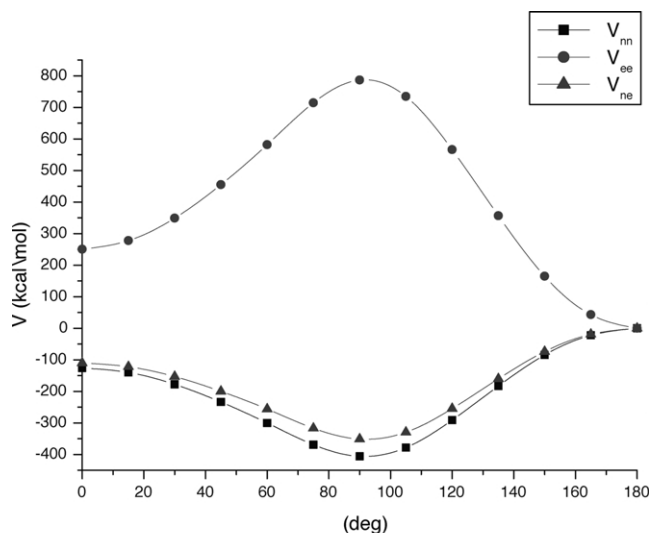

Figure 2. Torsional angle dependence of (a) the electrostatic terms V and (b) Lewis and non-Lewis energy terms for fully relaxed formic acid.

Table 2. The total energy, the Lewis and the hyperconjugation terms and the electrostatic components of the energy of formic acid for the rotation around the CO bond

τ	E_{tot} (a.u.)	ΔE_{tot} (kcal/mol)	E_{Lew} (a.u.)	ΔE_{Lew} (kcal/mol)	E_{del} (a.u.)	ΔE_{del} (kcal/mol)	E_{ex} (a.u.)	ΔE_{ex} (kcal/mol)
180	−189.795331	0.00	−189.521752	0.00	−0.273579	0.00	−17.918756	0.00
90	−189.774639	12.98	−189.527857	−3.83	−0.246782	16.82	−17.896799	13.78
0	−189.788892	4.04	−189.519164	1.62	−0.269727	2.42	−17.918057	0.44

τ	V_{nn} (a.u.)	ΔV_{nn} (kcal/mol)	V_{en} (a.u.)	ΔV_{en} (kcal/mol)	V_{ee} (a.u.)	V_{ee} (kcal/mol)
180	69.923871	0.00	−586.185340	0.00	138.716749	0.00
90	69.276915	−405.97	−548.931794	786.61	138.089920	−393.34
0	69.722991	−126.05	−585.786135	250.50	138.615235	−63.70

As one can see, the repulsive terms V_{ee} and V_{nn} favor the *cis* conformer of formic acid, not the *trans* one. These terms have the largest values for the most stable *trans* conformer, and decrease by 799 kcal/mol when going to the top of the barrier. On the other hand, the maximum of the attractive term V_{en} is at the barrier top. This value is lower by 786 and 250 kcal/mol, respectively, for *trans* and *cis* conformers. When the dihedral angle is changed from 180 to 90 ° as the barrier is traversed, V_{ne} becomes less negative. The $V_{nn}+V_{ee}$ term, however, becomes less positive, producing a net rise of energy dominated by decreased attraction. Thus, it is the interplay of the repulsive and attractive terms which makes the *trans* conformer the most stable one.

The electronic term V_{ee} is a sum of three terms: Coulomb repulsion energy E_{coul}, exchange energy E_{ex} and correlation energy E_c. These three terms change in a parallel way. The Coulomb term is the most important one, while the last two terms lower the value of electron repulsion, but no more than 15%.

We are now in a position to examine more fully the changes in the energy components as the barrier is traversed. Let us continue with the complementary analysis of the barrier by analyzing Lewis and hyperconjugation (non-Lewis) terms according to Eq. 3. If Lewis energy were the only term taken into account, the energy ordering of the conformers would be: $E_{top} < E_{cis} < E_{trans}$, which is opposite to the actual ordering of the total energy (see Figure 2b). However, delocalization energy of the conformers—called hyperconjugation energy in NBO model—increases in the same order as the total energy. This means that Lewis-like structure, without the hyperconjugation taken into account, would have opposite preferences. This demonstrates that electron delocalization of bonding to antibonding orbitals is the primary cause determining the barrier to rotation in formic acid, same as in ethane molecule.[4]

3.2. Ethanedial

The next molecule studied by us was ethanedial, which differs from formic acid by having the –COH group attached, instead of the –OH group, to the carbonyl group. The minimum energy conformation of this molecule is presented in Figure 1. The *trans* conformer is the global minimum on the molecular energy profile with respect to a change of the dihedral angle τ (H1–C1–C2–H2). Its geometrical parameters calculated at B3LYP/aug-cc-pVDZ level are presented in Table 1. Table 3 contains the total energies and the relative energy terms for different conformers.

The rotation barrier in ethanedial can be classified as repulsive. Inspection of Table 3 shows that the increase of the R term during intramolecular rotation is faster than the decrease of the A term, $|\Delta R| > |\Delta A|$. The relative total energy and the energy decomposition are shown in Figure 3a. The sum of the repulsive energy ($V_{ee}+V_{nn}$) is minimal for the *trans* conformer. On the other hand, the attractive component V_{en} has the lowest absolute value for the *trans* conformer. So, it is evident that the repulsive interactions strongly favor the *trans* conformation.
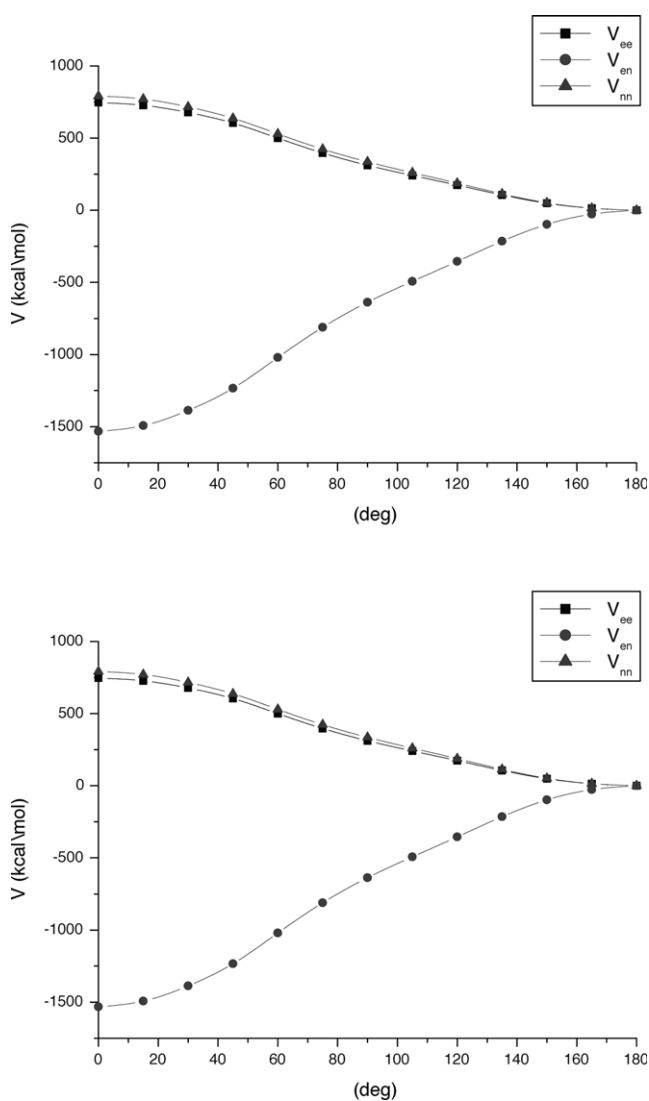

Figure 3. Torsional angle dependence of (a) the electrostatic terms V and (b) Lewis and non-Lewis energy terms for fully relaxed ethanedial.

Table 3. The total energy, the Lewis and the hyperconjugation terms and the electrostatic components of the energy of ethanedial for the rotation around the CC bond

τ	E_{tot} (a.u.)	ΔE_{tot} (kcal/mol)	E_{Lew} (a.u.)	ΔE_{Lew} (kcal/mol)	E_{del} (a.u.)	ΔE_{del} (kcal/mol)	E_{ex} (a.u.)	ΔE_{ex} (kcal/mol)
180	−227.856668	0.00	−227.569961	0.00	−0.286706	0.00	−21.843461	0.00
90	−227.847750	5.60	−227.566952	1.89	−0.28709	3.71	−21.842403	0.274
0	−227.849268	4.64	−227.550227	12.38	−0.299041	−7.74	−21.840054	0.289

τ	V_{nn} (a.u.)	ΔV_{nn} (kcal/mol)	V_{en} (a.u.)	ΔV_{en} (kcal/mol)	V_{ee} (a.u.)	V_{ee} (kcal/mol)		
180	101.573693	0.00	−737.536366	0.00	181.623392	0.00		
90	102.070044	311.46	−738.553006	−637.95	182.157878	335.39		
0	102.762216	745.81	−739.97875	−1532.62	182.885187	791.79		

In order to investigate the energetic preference of the *trans* form over the *cis* one we have carried out the NBO analysis, presented in Figure 3b. This figure shows that the hyperconjugative stabilization is the largest for the dihedral angle equal 0 °. If only that energy were taken into account, the energy ordering should be: $E_{cis} < E_{trans} < E_{top}$, which means that the delocalization of electron density favors the *cis* structure. On the other hand, the Lewis energy favors the *trans* conformer for this molecule. However, the Lewis energy term does not describe the energy sequence properly (the value for the top-of-the barrier conformer is smaller than for the *cis* one). The stabilization of the molecule and the energy ordering of the *trans*, *cis* and top-of-the barrier conformers is determined therefore by the interplay between both Lewis and hyperconjugation terms.

3.3. Glycolaldehyde

The third molecule investigated by us in this paper is glycolaldehyde. It differs from the formic acid by having the $-CH_2COH$ group, instead of the $-OH$ group, attached to the carbonyl group. The global minimum, denoted as the Gc structure, is shown in Figure 1. This structure is stabilized by an intramolecular hydrogen bond involving the carbonyl oxygen and hydroxyl hydrogen. The second minimum under study, named Go-glycolaldehyde, is found for another structure presented in Figure 1. It differs from the global minimum Gc by the position of the $-OH$ group. Actually, there are more local minima on the PES of glyceraldehyde but there are the subject of other paper, where we discuss the potential energy surface and the spin–spin coupling constants for this molecule.[16] The selected optimized structural parameters at the B3LYP/aug-cc-pVDZ have been reported in Table 1 for Gc- and Go-glycolaldehyde structures. The energy difference between Gc and Go structures is 3.38 kcal/mol. We investigated the rotation about the CC bond changing the dihedral torsion angle τ=H1–C1–C2–H2 by 15 ° and carrying out the partial

geometry optimization starting from the structures Gc and Go. This results in two different rotation paths. Tables 4 and 5 present the total energy for the stable conformers on each pathway and for the transition state conformers at the top of the barriers for Gc- and Go-glycolaldehyde structures.

Let us discuss first the terms of the energy in Eq. 1. The data of Table 4 are displayed in Figure 4 and the data of Table 5 are shown in Figure 5. The figures present increments of the total energy and the potential energy components. When the dihedral angle τ in Gc-glycolaldehyde structure is changed from 60 to 210 ° (the barrier is traversed at 135 °) the V_{ne} term becomes less negative. The absolute value of the attractive ΔV_{ne} energy is lower by 2431 and 2449 kcal/mol at the barrier top (135 °) than at the most stable structure (60 °) and the second minimum conformer at 210 ° The repulsive terms ($V_{ee}+V_{nn}$) however, become less positive, producing a net rise dominated by decreased attraction. So, for the rotation barrier of Gc-glycolaldehyde the relation is $|\Delta A| > |\Delta R|$, i.e. the barrier is classified as attractive. Contrary to that, the barrier to rotation for the structure Go-glycolaldehyde should be classified as repulsive, because the phases of the two components are reversed. The term V_{ne} becomes more negative when the dihedral angle τ is changed from 120 to 240 °, but the sum of repulsive terms becomes more positive, producing a net rise in energy dominated by increased repulsion: $|\Delta R| > |\Delta A|$.

For the further understanding of the conformation preference let us analyse the decomposition of the total energy to Lewis and hyperconjugation terms. The minimum of the Lewis energy (the highest absolute value) and the maximum of the hyperconjugation term are close to the barrier top at 135 ° (Figure 4b) for the Gc-glycolaldehyde. This means that the hyperconjugation term, not the Lewis energy, is the most important for the energetic ordering of the total energy $E_{60} < E_{210} < E_{top}$. It should be stressed that only the attractive potential V_{ne} is involved in hyperconjugative interactions.

Table 4. The total energy, the Lewis and the hyperconjugation terms and the electrostatic components of the energy of Gc-glycolaldehyde for the rotation around the CC bond

τ	E_{tot} (a.u.)	ΔE_{tot} (kcal/mol)	E_{Lew} (a.u.)	ΔE_{Lew} (kcal/mol)	E_{del} (a.u.)	ΔE_{del} (kcal/mol)	E_{ex} (a.u.)	ΔE_{ex} (kcal/mol)
60	−229.081908	0.00	−228.828213	0.00	−0.253696	0.00	−22.422489	0.00
135	−229.073038	5.57	−228.845153	−10.63	−0.227885	16.19	−22.416268	3.90
210	−229.076213	3.57	−228.837830	−6.03	−0.238383	9.61	−22.416653	3.66

τ	V_{nn} (a.u.)	ΔV_{nn} (kcal/mol)	V_{en} (a.u)	ΔV_{en} (kcal/mol)	V_{ee} (a.u.)	V_{ee} (kcal/mol)		
60	118.635721	0.00	−774.382778	0.00	199.213216	0.00		
135	116.682265	−1225.81	−770.508041	2431.43	197.301846	−1199.40		
210	114.726324	−2453.18	−766.604134	4881.17	195.334604	−2433.86		

Table 5. The total energy, the Lewis and the hyperconjugation terms and the electrostatic components of the energy of Go-glycolaldehyde for the rotation around the CC bond

τ	E_{tot} (a.u.)	ΔE_{tot} (kcal/mol)	E_{Lew} (a.u.)	ΔE_{Lew} (kcal/mol)	E_{del} (a.u.)	ΔE_{del} (kcal/mol)	E_{ex} (a.u.)	ΔE_{ex} (kcal/mol)
120	−229.076515	0.00	−228.844111	0.00	−0.232404	0.00	−22.418822	0.00
240	−229.068604	4.96	−228.839481	2.90	−0.229124	2.06	−22.415421	2.13
300	−229.073930	1.62	−228.821791	14.01	−0.252140	−12.38	−22.417789	0.65

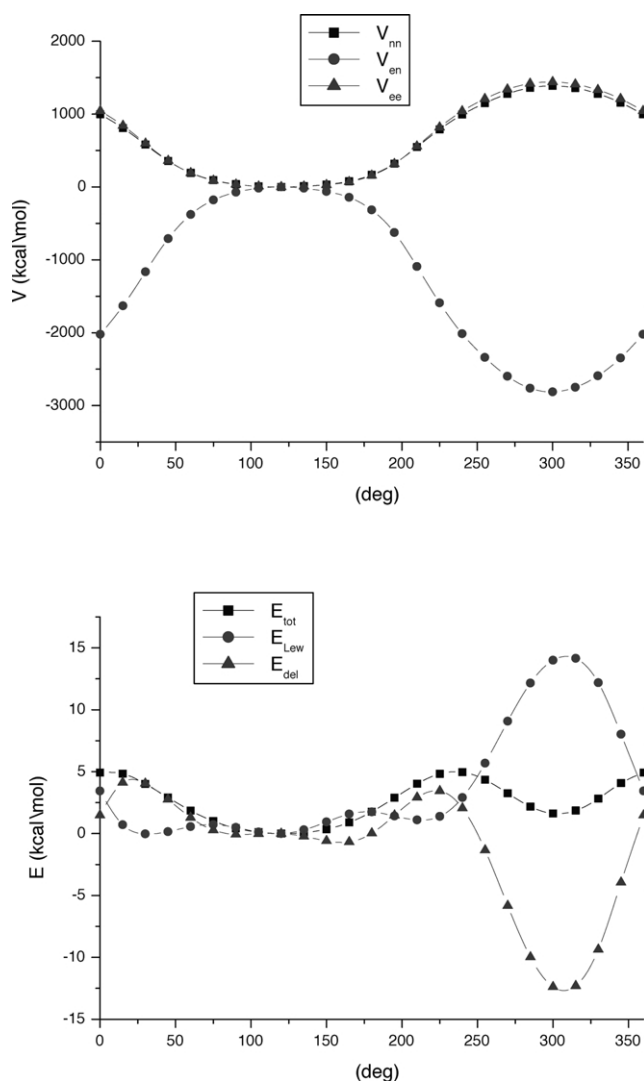| τ	V_{nn} (a.u.)	ΔV_{nn} (kcal/mol)	V_{en} (a.u)	ΔV_{en} (kcal/mol)	V_{ee} (a.u)	V_{ee} (kcal/mol)		
120	115.000090	0.00	−767.219062	0.00	195.671916	0.0		
240	116.583292	993.47	−770.427780	−2013.50	197.330602	1040.84		
300	117.211512	1387.68	−771.699387	−2811.45	197.970268	1442.24		

Figure 4. Torsional angle dependence of (a) the electrostatic terms *V* and (b) Lewis and non-Lewis energy terms for fully relaxed Gc-glycolaldehyde.

Figure 5. Torsional angle dependence of (a) the electrostatic terms *V* and (b) Lewis and non-Lewis energy terms for fully relaxed Go-glycolaldehyde.

4. Conclusions

One can conclude that it is the reduction of the attractive electron-nuclear component which determines the structure of Gc-glycolaldehyde. Contrary to that, neither Lewis nor hyperconjugation alone can reproduce the sequence of the total energy in the case of the Go-glycolaldehyde structure (Figure 5b): $E_{120} < E_{300} < E_{top}$. This data illustrate the importance of the interplay of both Lewis and hyperconjugation components, i.e. the importance of the steric as well as the hyperconjugation origin of the conformational preference of the Go-glycolaldehyde structure.

Finally, we notice that the graph in Figure 4b is essentially the same as that in Figure 2b. The decomposition of the energy of the Gc-glycolaldehyde structure does not differ from that in the formic acid: the change of the attractive term (which outweighs the change of the repulsive term) and the hyperconjugation energy are the leading factors. The results in Table 5 suggest also that there is no fundamental difference in the decomposition of the electrostatic energy terms. Similarly, the graph in Figure 5b is essentially the same as the one in Figure 3b, what means the same pattern of the energy decomposition occurs for the ethanedial and for the Go-glycolaldehyde.
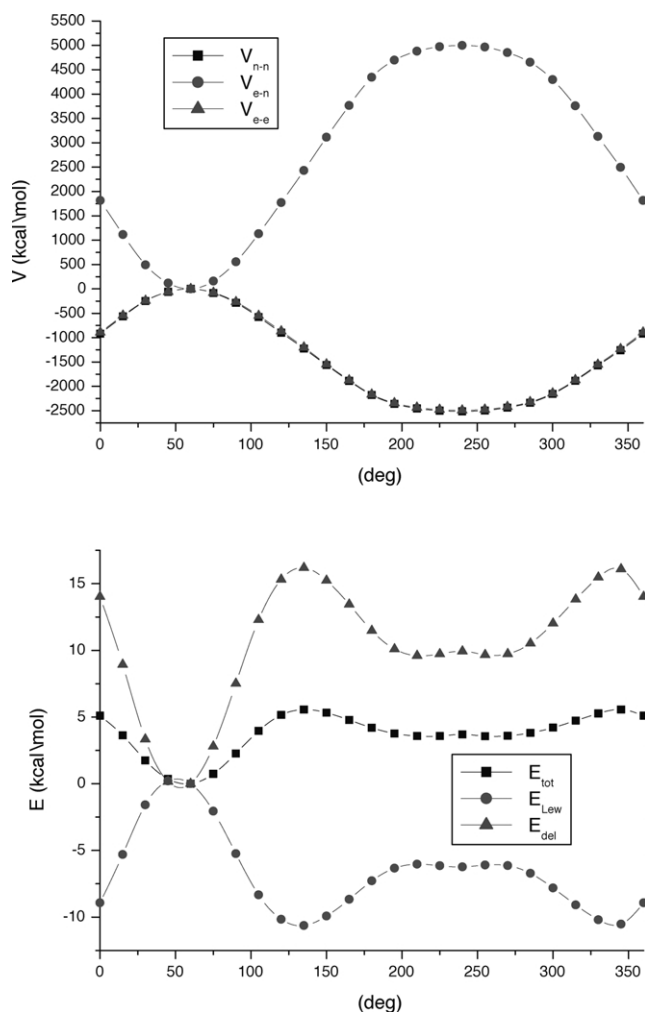
In this paper, we determined the rotational barriers for a sequence of three molecules with the carbonyl group by ab initio calculations. The results can be summarized as follows:

(1) Decomposition of the total energy into attractive and repulsive components allows for a physical interpretation of the barrier to rotation. Formic acid and Gc-glycolaldehyde have been shown to have a rotational barrier that is predominantly attractive, i.e. arises mainly from reduction of the attractive interaction rather than an increase in the repulsive one. The situation is opposite in ethanedial and Go-glycolaldehyde, where the energy rise is dominated by the increased repulsion. We would like to stress that the nature of the rotation barrier around the C–C bond is completely changed when the –OH group assumes a different conformation.

(2) The predominantly attractive nature of the rotational barrier in formic acid and Gc-glycolaldehyde was confirmed by the analysis of the Lewis and non-Lewis components of the total energy. The prevalent factor determining the nature of this barrier is the loss of the

hyperconjugation when rotation from the most stable to the less stable conformer occurs. This contrasts with the dominance of repulsion for ethanedial and Go-glycolaldehyde barriers, which is due to the balance between the Lewis and the hyperconjugation energetic terms. Neither Lewis nor the hyperconjugation alone can reproduce the sequence of the total energy of these conformers.

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