

*Original Investigations***An *ab initio* Study of the Keto–Enol Tautomerism**

Wolf-Eckart Noack

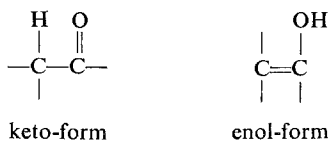
Institut für Theoretische Chemie der Universität Stuttgart, Pfaffenwaldring 55, D-7000 Stuttgart 80, Federal Republic of Germany

The keto–enol tautomerism is studied using an approximative HF method outlined in the appendix. The following results are obtained: (1) The experimentally observed alternance of ΔG in acyclic monoketones could not be reproduced. (2) The stabilization of C=C double bonds, especially of conjugated double bonds, by CH₃– or –CH₂– groups is responsible for the observed difference between acyclic and cyclic 1.2-diketones, e.g. for the different enol content of diacetyl and cyclopentane-1.2-dione. (3) The enols of 1.2-diketones contain a hydrogen bond which differs from the hydrogen bond in enols of 1.3-diketones. (4) A system of two conjugated C=O double bonds is not favoured compared to a system of two C=O bonds which are separated by one (or more) –CH₂– group. (5) 5-ring enols with a C=C double bond in the ring are more stable than one would expect by an energy estimation from acyclic compounds.

Key words: Keto–enol tautomerism – Hyperconjugation – Hydrogen bonds

1. Introduction

In the present paper the keto–enol tautomerism



of several molecules is studied using an approximative HF method which is outlined in the appendix. By theoretical methods one can calculate the ground state energies E of both tautomeric forms. Neglecting zero point vibration energies,

one can compare the value $\Delta KE = E(\text{enol}) - E(\text{ketone})$ with the reaction enthalpy in the gas phase of 0 K. However, the experimental ΔG and ΔH values of keto-enol reactions have been mainly determined at room temperature in the liquid phase. Therefore it seems to be impossible to reproduce such experimental results by *ab initio* calculations. But one can try – and this is the aim of the present work – to find out relations between the calculated ΔKE -values and the structure of the molecules. Relations between experimental data and the molecular structure are already discussed by Wheland [1], but the interpretation of these results is not in all cases satisfying. Therefore it should be useful to treat this problem by *ab initio* calculations which can give a better insight where direct experiments are not possible.

2. Experimental Results and Their Interpretation

Table 1 contains the amount of the enol form in per cent at the equilibrium and the corresponding ΔG values of some ketones and diketones measured by several authors at room temperature. The experimental results and their interpretation given in the literature are outlined in [1] and are briefly summarized in the following four subsections.

Table 1. In the first column are the experimentally measured enol contents in percent. Behind the slash is the corresponding ΔG value in kcal/mole for $T = 293$ K. For several molecules as acetone, acetylacetone, diacetyl and the ring compounds exist two enol forms with the same geometry and the same energy. This lowers ΔG by $-T\Delta S = -R \cdot T \cdot \ln 2 \approx 0.4$ kcal/mole. This value should be added to the *ab initio* ΔKE values of the second column given in kcal/mole. The notations of the molecules are given in Sect. 7, Fig. 1a-d

| Molecule | % Enol/ ΔG | ΔKE | $\Delta KE - \Delta G$ |
|------------------------------|-----------------------------|-------------|------------------------|
| acetone (K2) | 1.5 D - 4/+7.8 ^a | 18.8 | 11.0 |
| | 2.5 D - 4/+7.5 ^b | | 11.3 |
| methyl-ethyl-ketone (K3) | 1.2 D - 1/+3.9 ^a | 15.6 | 11.7 |
| methyl-propyl-ketone (K4) | 8.6 D - 3/+5.5 ^a | 13.8 | 8.3 |
| methyl-butyl-ketone (K5) | 1.1 D - 1/+4.0 ^a | 13.8 | 9.8 |
| | 8.8 D - 2/+4.1 ^a | | 16.6 |
| cyclopentanone (K6) | 4.8 D - 3/+5.9 ^c | 20.7 | 14.8 |
| | 1.2 D - 0/+2.6 ^a | | 13.0 |
| cyclohexanone (K7) | 2.0 D - 2/+4.9 ^c | 15.6 | 10.7 |
| | 7.6 D + 1/-0.7 ^a | | 4.5 |
| acetylacetone (K12b) | 8.0 D + 1/-0.8 ^g | 3.8 | 4.6 |
| | 9.5 D + 1/-1.7 ^f | | 5.5 |
| | 1.1 D - 0/+2.6 ^a | | 14.4 |
| diacetyl (K18a) | 5.6 D - 3/+5.7 ^c | 14.4 | 8.7 |
| | 9.9 D + 1/-2.7 ^d | | 8.2 |
| cyclopentane-1.2-dione (K20) | 4.0 D + 1/+0.2 ^d | 5.0 | 4.8 |
| cyclohexane-1.2-dione (K21) | 9.5 D + 1/-1.7 ^e | 10.6 | 12.3 |
| cyclohexane-1.3-dione (K16) | | | |

^a Ref. [2]. ^b Ref. [3]. ^c Ref. [4]. ^d Ref. [5]. ^e Ref. [6].

^f Ref. [7]; only measurement performed in the gas phase. ^g Ref. [8].

2.1. Ketones Containing Two Carbonyl Groups

The percentage of the enol form is considerably large if the ketone contains two carbonyl groups, namely in 1.3-diketones and in cyclic 1.2-diketones. However, the percentage is small in acyclic 1.2-diketones.

The high percentage of the enol form of 1.3-diketones is explained by two factors. Firstly, the enol form (not the keto form) contains a system of conjugated double bonds. Secondly, the enol form of acyclic 1.3-diketones has a hydrogen bond leading to a chelate ring:



Both effects lower the energy of the enol form. However, in 1.2-diketones there exist conjugated double bonds in the keto and the enol form



and thus lower the energy of both forms.

The existence of a hydrogen bond in the enol form of 1.2-diketones is not assumed in the literature. Wheland [1] states that for example diacetyl exists largely in the keto form probably because its enol form is prevented from having hydrogen bonds by steric requirements. This is one point which is investigated in the present work. On the other hand it is surprising that the cyclic 1.2-diketones exist largely in the enol form (cf. Table 1). Wheland [9] suggested that the reason for the different behaviour of the acyclic and the cyclic 1.2-diketones is that the former ketones can have the stable *trans* arrangement, whereas the latter cannot. If this would be the only reason, one should expect that the calculated ΔKE value of the acyclic compound with the *cis* arrangement and the cyclic 1.2-diketone should resemble each other.

2.2. Ring Systems

Cyclic compounds favour the enol form considerably. Look for example at the different values (Table 1) for acetone on the one hand and cyclopentanone or cyclohexanone on the other hand. The difference between cyclic and acyclic 1.2-diketones is already discussed in Sect. 2.1.

The explanation given in the literature is the following. Acyclic compounds are becoming more rigid by the enolization thus reducing the reaction entropy ΔS and the amount of the enol form. However, in cyclic compounds the keto form is rigid too, so that the development of the C=C double bond cannot influence ΔS considerably. Perhaps this explanation proves true in many cases, but it is doubtful whether this effect plays the dominant part in all cases. For example Briegleb and Strohmeier [7] could show that the value $T \cdot \Delta S$ of acetylacetone is only -0.18 kcal/mole at 273 K.

2.3. Influence of Ring Size

The percentage of the enol form alternates with the size of the ring systems. This could be observed by Schwarzenbach *et al.* [10] and Strohmeier *et al.* [11]. Strohmeier *et al.* [11] showed that ΔH and not $T \cdot \Delta S$ is responsible for the alternation. This behaviour cannot be studied here because *ab initio* calculations of these molecules would be too time consuming.

2.4. Influence of the Chain Length

The same alternating character can be observed at the acyclic monoketones. The first four examples of Table 1 show that the amount of the enol form alternates with increasing length of the chain. It is not clear whether ΔH , ΔS or intermolecular interactions are responsible for this alternation.

3. Method of Calculation

The ground state energies of the molecules are calculated using an approximative HF method which is described in the appendix. The level of approximation is **b** (cf. appendix). The calculations are performed with the STO-3G basis set of Hehre and Pople [13]. The geometry of the molecules is determined by the standard values of Pople and Gordon [14]. Exceptions, especially for the cyclic compounds, are given in Sect. 5.

To estimate the error due to the neglect of correlation energy, the "local spin density correlation energy" of acetaldehyde and its enol form is calculated using a method developed by Stoll [15]. The correlation energies are -0.719 a.u. for the keto- and -0.720 a.u. for the enol form and thus lead to a negligible correction for ΔKE . One can suppose that the small difference of these two correlation energies will be roughly the same for the other compounds because in all keto-enol reactions the same changes occur.

The error in the energy of the approximative method compared to corresponding HF calculations with no approximations was extensively tested and is given in the appendix. For example the error of ΔKE for the keto-enol reaction of acetaldehyde is 3 kcal/mole. Again one can suppose that this error is roughly the same in all other reactions because the type of reaction is always the same. Test calculations for several keto-enol reactions are also carried out at level **a** (cf. appendix) and lead to nearly the same ΔKE values.

4. Estimation of Binding Energies

Consider the reactions $R_i-H + H-R_i \rightarrow R_i-R_i + H_2$ for different groups R_i ($i = 1, n$). If the binding energy of a molecule **A** is denoted by $B(\mathbf{A})$ one can write for the reaction energy $H_i = B(H_2) + B(R_i-R_i) - 2B(R_i-H)$ and for the energy difference Δ_i between the linked and the unlinked molecules of the i th reaction: $\Delta_i = B(R_i-R_i) - 2B(R_i-H)$. With the "linkage energy" Δ_1 of the first reaction

and the values $B(R_i-H)$ it is possible to make an estimation for the energy of the molecule R_i-R_i by: $B(R_i-R_i)_{\text{est}} = 2B(R_i-H) + \Delta_1$. For the difference between the directly calculated and the estimated energy of R_i-R_i one obtains: $B(R_i-R_i) - B(R_i-R_i)_{\text{est}} = H_i - H_1 = \Delta_i - \Delta_1$. Thus this difference is a measurement for the different influence of R_i and R_1 on the reaction energy H or the linkage energy Δ , respectively. If one estimates the energies of all R_i-R_i by using always the same increment Δ_1 , the linkage of the first reaction may be regarded as a "reference linkage". The choice of such a reference linkage is of course arbitrary. The same comparison between the estimated and the directly calculated energy is applied to the molecules of this work. For this purpose some reference linkages and their increments Δ are given in Table 2. With one or more of them one can build up large molecules out of smaller ones. According to this one can estimate their energies from the energies of the small molecules and the increments Δ of Table 2. The difference $B_{\text{calc}} - B_{\text{est}}$ is called difference value in this work and gives information as to what extent the linkages used to build up the large molecule differ from the reference linkages. The following example demonstrates the use of such estimations. Cyclopentane can be constructed out of pentane by the linkage L_4 of Table 2. According to that the binding energy of cyclopentane can be estimated to be $B(\text{cyclopentane})_{\text{est}} = B(\text{pentane}) + \Delta_4$. However, this estimated energy is lower by about 9 kcal/mole than the calculated binding energy. The reason is that in the cyclopentane molecule the hydrogen atoms are forced to take the eclipsed conformation whereas for the acyclic compound, which is used for the energy estimation, the more favourable staggered conformation is chosen.

If one estimates the binding energies as described above one must guarantee that the geometry of the compounds which are compared is nearly equal in order to make a transference from the smaller to the larger compound possible. For example, one can estimate the energy of cyclopentene from the calculated energy of *cis*-2-butene and the energy Δ_5 of the linkage L_5 (cf. Table 2) which closes the acyclic

Table 2. The linkages $L_1 - L_5$ and their energies $\Delta_i =$ sum of molecular energies on the r.h.s. - sum of molecular energies on the l.h.s. L_5 is a combination of L_1 and L_4 . The linkage energies refer to $R = -\text{CH}_3$ or $-\text{CH}_2-\text{CH}_3$ and to $X = Y = Z = \text{H}$. With these linkages one can construct large molecules out of small molecules for any R, X, Y and Z

| | | |
|--------|--|---------------------|
| $L_1:$ | $\text{R}-\text{CH}_3 \longrightarrow \text{R}-\text{CH}_2-\text{CH}_3$ | $\Delta_1 = -0.378$ |
| $L_2:$ | $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array} \longrightarrow \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{CH}_3 \end{array}$ | $\Delta_2 = -0.381$ |
| $L_3:$ | $\begin{array}{ccc} \text{X} & & \text{H} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{Y} & & \text{Z} \end{array} \longrightarrow \begin{array}{ccc} \text{X} & & \text{CH}_3 \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{Y} & & \text{Z} \end{array}$ | $\Delta_3 = -0.385$ |
| $L_4:$ | $\text{R}-\text{CH}_3 + \text{CH}_3-\text{R} \longrightarrow \text{R}-\text{CH}_2-\text{CH}_2-\text{R}$ | $\Delta_4 = +0.143$ |
| $L_5:$ | $\text{R}-\text{CH}_3 + \text{CH}_3-\text{R} \longrightarrow \text{R}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{R}$ | $\Delta_5 = -0.235$ |

system to a ring. For the estimated energy one obtains: $B(\text{cyclopentene})_{\text{est}} = B(\text{cis-2-butene}) + \Delta 5$. If one wants to know to what extent this closure differs from the linkage L_5 in Table 2, which refers to acyclic systems, one must reduce the angle α at the —C=C— double bond in *cis*-2-butene from its equilibrium value of about 120° to the equilibrium angle of cyclopentene which is about 110° . However, for such a small angle there exists a repulsive interaction between the two CH_3 -groups in *cis*-2-butene which does not exist in the cyclic compound. To avoid this interaction the estimation is performed with *trans*-2-butene. This seems to be reasonable because the energy difference between the *cis*- and *trans*- forms is very small for $\alpha = 120^\circ$ so that one can expect it to be small also for $\alpha \approx 110^\circ$ if one neglects the repulsive interaction in the *cis* compound. In the same way as outlined here, the estimations for the other cyclic enols are performed.

5. Geometry of the Molecules

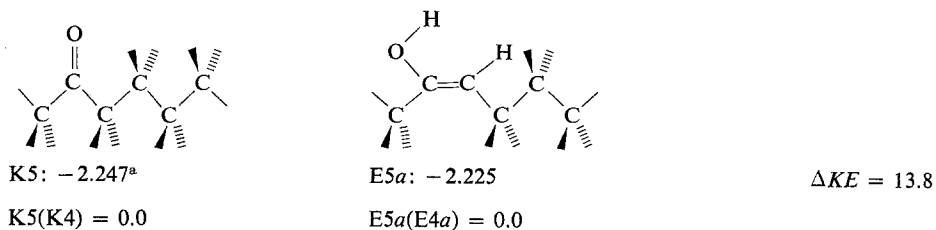
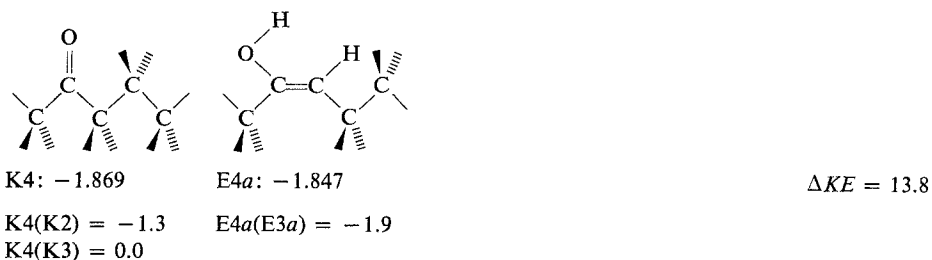
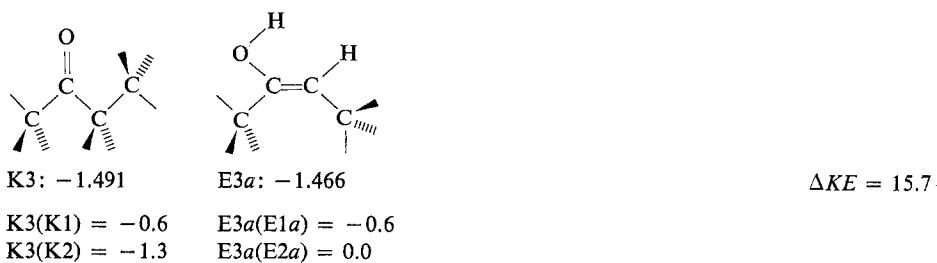
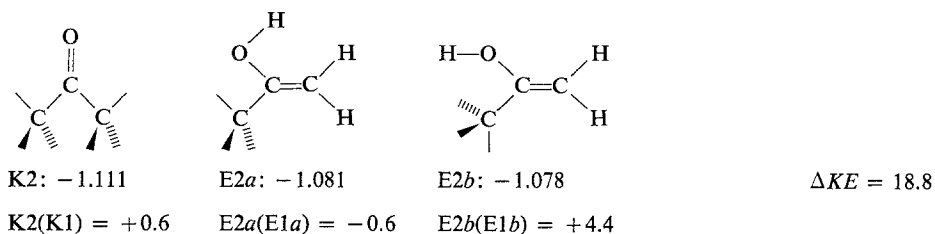
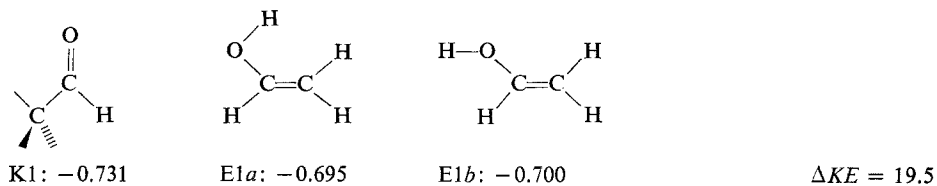
Exceptions from the standard geometric parameters of Pople and Gordon [14] occur especially in the cyclic compounds. To describe their conformations the C atoms of the ring-skeletons are numbered clockwise and the atom with the number 1 is given in Fig. 1*a-d* for each cyclic compound. Their conformations are as follows (K = keto-form, E = enol-form, notations are given in Fig. 1*a-d*): K6 = cyclopentanone: twisted conformation, C3 is above and C4 is below the plane $P(\text{C1, C2, C5})$; E6: C4 looks out of the plane $P(\text{C1, C2, C3, C5})$; K7 = cyclohexanone: chair conformation; E7: twisted conformation, C4 is above and C5 is below the plane $P(\text{C1, C2, C3, C6})$; K15 = cyclopentane-1.3-dione: planar; E15: planar; K16 = cyclohexane-1.3-dione: chair conformation; E16: C4 looks out of the plane $P(\text{C1, C2, C3, C5, C6})$; K20 = cyclopentane-1.2-dione: C4 looks out of the plane $P(\text{C1, C2, C3, C5})$; E20: planar; K21 = cyclohexane-1.2-dione: twisted conformation, C4 is above and C5 below the plane $P(\text{C1, C2, C3, C6})$; E21: C4 looks out of the plane $P(\text{C1, C2, C3, C5, C6})$; cyclopentene: geometry as E6.

The distances are standard values taken from [14]. The angles at the —C=C— double bonds are 110° – 111.5° in the five-ring compounds and 123° in six-ring compounds. The C—C—C single bond angles vary from 103.5° to 109° in five-ring compounds and from 105.5° to 111° in six-ring compounds. Test calculations showed that the deviation of these angles from the tetrahedral one does not raise the energy significantly. The geometry of the hydrogen atoms in the CH_2 group can be described as follows if one denotes the C atom of the CH_2 group by C1 and the two adjacent C atoms by C2 and C3. The angle $\angle(\text{H, C1, H})$ is tetrahedral and the plane $P(\text{H, C1, H})$ is vertical to the plane $P(\text{C1, C2, C3})$. The sectional line of these two planes coincides with that line which bisects the angle $\angle(\text{C2, C1, C3})$.

In the acyclic compounds there are the following deviations from the standard

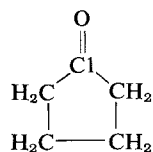
geometry. The C—H distance in $\begin{array}{c} \text{O} \\ || \\ \text{C—H} \end{array}$ is chosen 1.114 \AA [16]. Moreover the angles of those enols which correspond to acyclic 1.3-diketones—these are the molecules E10*a*, E10*b*, E11*a*, E11*b* and E12*a* of Fig. 1*b*—are so altered that the distance

Fig. 1a. Structure formulas of the compounds of group *A* and their notation. Behind the notation is placed the binding energy in a.u. ΔKE values are given in kcal/mole and refer to the most stable conformation of the keto and enol form. The difference values below the binding energies are given in kcal/mole. Their denotation is explained in the text



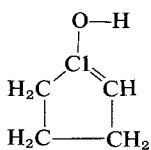
^a This value is estimated from *B*(K4). See Sect. 7.1

Fig. 1a (continued)



K6: -1.727

K6(K4) = -0.6



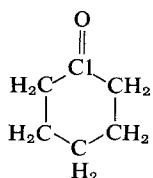
E6: -1.694

E6(E3a) = +4.4

E6(E4a) = +6.3

 $\Delta KE = 20.7$

To take into account the different angles for the estimation one has to subtract 11 kcal/mole from the difference values of E6. By this value the energy of *trans*-2-butene is raised if α (cf. 7.10) is reduced from 120° to 111°

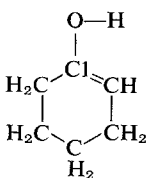


K7: -2.110

K7(K2) = -5.0

K7(K4) = -3.8

K7(K6) = -3.1

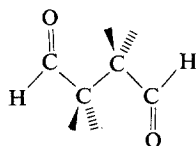


E7: -2.085

E7(E3a) = -3.8

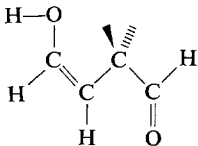
E7(E4a) = -1.9

E7(E6) = -8.2

 $\Delta KE = 15.7$ 

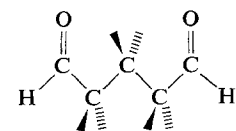
K8: -1.320

K8(K1) = -0.6



E8b: -1.295

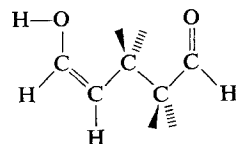
E8b(K1, E1b) = 0.0

 $\Delta KE = 15.7$ 

K9: -1.698

K9(K1) = -0.6

K9(K8) = 0.0



E9b: -1.672

E9b(E8b) = +0.6

 $\Delta KE = 16.3$

From E2a, E3a and E4a the conformations E2c, E3c and E4c are calculated with H of -OH looking out of the plane (dihedral angle = 90°). The energies are: $B(E2c) = -1.074$, $B(E3c) = -1.460$ and $B(E4c) = -1.839$ a.u.

Fig. 1b. Structure formulas of the compounds of group *B* and their notation. For the ΔKE and difference values see Fig. 1a. In K10*b*, K11*b* and K12*b* the —CHO group is rotated by $\beta = 90^\circ$ about the C—C linkage out of the plane

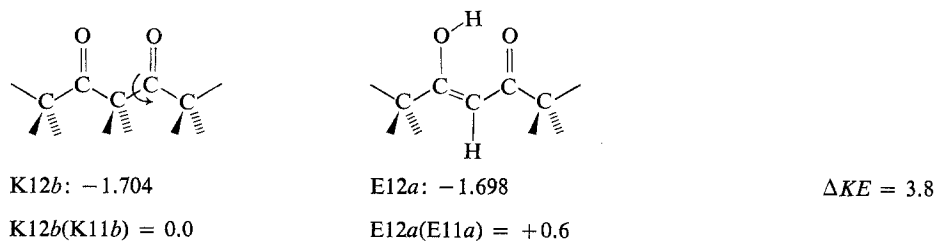
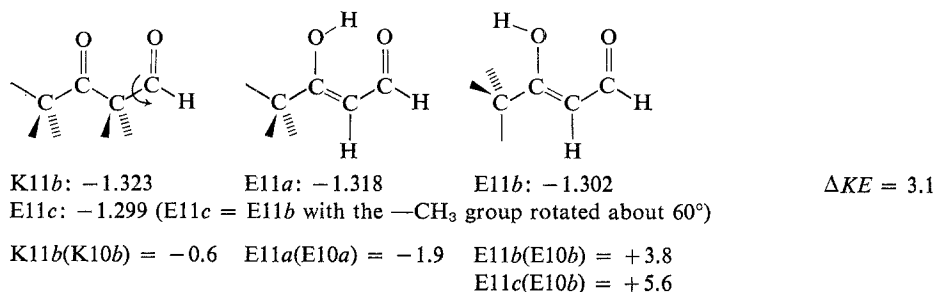
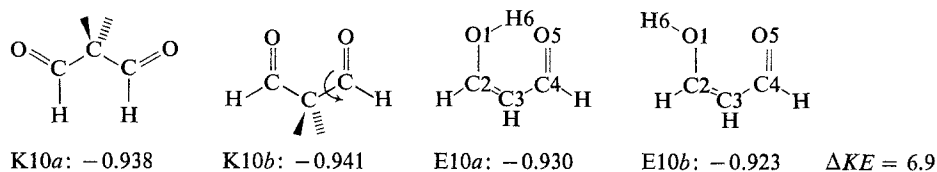


Fig. 1c. Structure formulas of the compounds of group *C* and their notation. For ΔKE and difference values see Fig. 1a

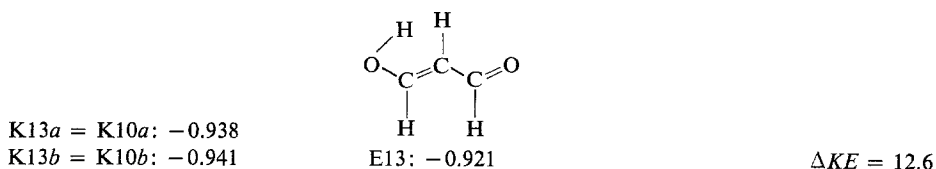
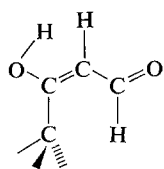
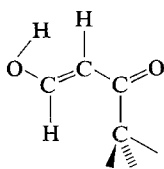


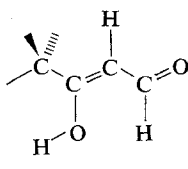
Fig. 1c (continued)



E14a: -1.303



E14b: -1.298



E14d: -1.279

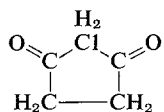
 $\Delta KE = 12.6$

(E14d has the geometry of the five-ring system E15)

The binding energy of E14a with the six-ring geometry of E16 is -1.306

K14b = K11b: -1.323

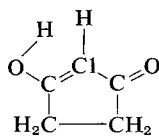
E14a(E13) = +1.9 E14b(E13) = +2.5



K15: -1.562

K15(K13b) = -1.3

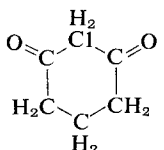
K15(K12b) = -0.6



E15: -1.547

E15(E13) = -1.9 E15(E14a) = -3.8

E15(E14b) = -4.4 E15(E14d) = -18.8

 $\Delta KE = 9.4$ 

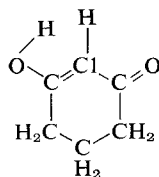
K16: -1.945

K16(K12b) = -3.8

K16(K13b) = -4.4

K16(K15) = -3.1

E16(E14a with the same geometry as E16) = -3.8

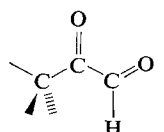


E16: -1.928

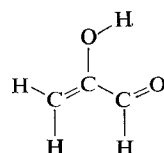
E16(E13) = -3.8

E16(E14a) = -5.6

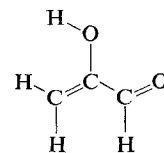
E16(E15) = -1.9

 $\Delta KE = 10.7$ Fig. 1d. Structure formulas of the compounds of group C and their notation. For ΔKE and difference values see Fig. 1a

K17: -0.938



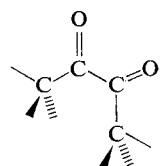
E17a: -0.918



E17b: -0.912

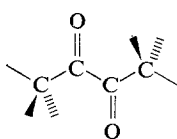
 $\Delta KE = 12.6$

Fig. 1d (continued)



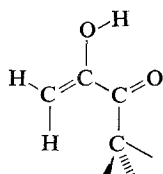
K18a: -1.321

K18a(K17) = -1.3



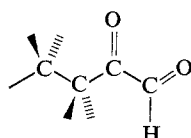
K18b: -1.322

K18b(K17) = -1.9



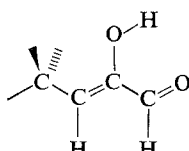
E18: -1.299

E18(E17a) = 0.0

 $\Delta KE = 14.4$ 

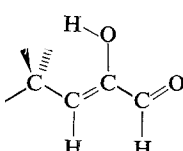
K19: -1.318

K19(K17) = -1.3



E19a: -1.305

E19a(E17a) = -1.3

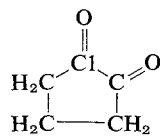


E19b: -1.293

E19b(E17b) = +2.5

Binding energy of E19a with the five-ring geometry: -1.278

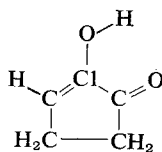
Binding energy of E19a with the six-ring geometry: -1.303

 $\Delta KE = 8.2$ 

K20: -1.555

K20(K17) = -0.6

K20(K18a) = +0.6

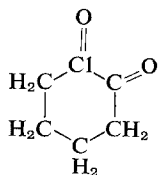


E20: -1.542

E20(E17a) = -0.6

E20(E19a) = +0.6

E20(E19a with five-ring geometry) = -16.3

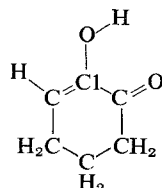
 $\Delta KE = 8.2$ 

K21: -1.931

K21(K17) = +0.6

K21(K18a) = +1.9

K21(K20) = +1.3



E21: -1.923

E21(E17a) = -2.5 E21(E18) = -2.5

E21(E19a) = -1.3 E21(E20) = -2.5

E21(E19a with six-ring geometry) = -2.5

 $\Delta KE = 5.0$

H6–O5 is increased (the numbering of these atoms is given in E10a and E10b). This lowers the energy considerably compared to that nuclear arrangement which results if the standard geometric parameters are used. The new angles have the values: $\angle(\text{H6}, \text{O1}, \text{C2}) = 110^\circ$; $\angle(\text{O1}, \text{C2}, \text{C3}) = 124^\circ$; $\angle(\text{C2}, \text{C3}, \text{C4}) = 122^\circ$; $\angle(\text{C3}, \text{C4}, \text{O5}) = 124^\circ$. The new distance H6–O5 is 1.87 Å.

6. Results

The compounds are divided into four groups A, B, C and D and their structural formulas are presented in Figs. 1a–1d. The notation of the molecules is as follows: *Ki* or *Ei* refers to the keto or enol form of the *i*th reaction. Different conformations of a molecule are denoted by the suffix *a*, *b*, *c* etc. Below the structural formulas are placed the *ab initio* calculated binding energies *B* in a.u. On the right side are the ΔKE values for every keto–enol reaction in kcal/mole. These values $\Delta KE = B(\text{enol}) - B(\text{ketone})$ always refer to those conformations of the keto and enol form with the lowest energy. Below the binding energies are placed the difference values $B - B_{\text{est}}$ in kcal/mole ($B = B_{\text{calc}}$) and are denoted in the following manner. If for example $B(\text{Kj})_{\text{est}}$ is estimated from $B(\text{Ki})$ as described in Sect. 4, the difference $B(\text{Kj}) - B(\text{Kj})_{\text{est}}$ is expressed by $\text{Kj}(\text{Ki})$. Of special interest are all those cases where these values, which are here called difference values, deviate strongly from zero.

Fig. 1a contains monoketones and also those diketones where the carbonyl groups are separated from each other by more than one $-\text{CH}_2-$ group. The calculated energy ΔKE of the reaction acetaldehyde \rightarrow vinyl alcohol ($\text{K1} \rightarrow \text{E1}$) is about 20 kcal/mole. An estimation of this value by the method of Klages and Franklin [1] leads to a value of 13 kcal/mole. If one assumes an error of ± 3 kcal/mole for this estimation, the maximal error of the *ab initio* calculation is 10 kcal/mole. By this amount the calculated ΔKE value is too large. Assuming the same error for all the other keto–enol reactions, one can expect that there will be more than 50% enol if the calculated ΔKE value is less than 10 kcal/mole. This value should be only a help for a rough orientation.

The reaction energies ΔKE of group A are all larger than 10 kcal/mole. This means – in agreement with the experimental data of Table 1 – that the keto-form should be dominant. A further agreement with the experimental data is the result that the ΔKE values of the reactions 3, 4 and 5 are lower by 3–5 kcal/mole than the ΔKE value of reaction 2. However, the exceptional ΔKE value of cyclopentanone (K6) does not agree with the corresponding ΔG value of Table 1.

Figure 1b shows the structural formulas of 1.3-diketones and their enols which have a hydrogen bond and form a chelate ring. All ΔKE values are smaller than 10 kcal/mole so that one can expect the enol form to be dominant. This is valid for acetylacetone (K12b) (cf. Table 1). For the other compounds experimental data are not available.

Figure 1c also contains 1.3-diketones, acyclic and cyclic ones, but their enols do not have a hydrogen bond. The loss of the hydrogen bond causes the larger ΔKE values

of group *C* compared to group *B*. But nevertheless the ΔKE value of 10.6 kcal/mole for cyclohexane-1.3-dione (K16) means that its enol should exist at a considerable amount. This is in rather good agreement with the experimental value of 95% (cf. Table 1).

Figure 1*d* presents the group *D* consisting of 1.2-diketones and their enols. Note that—in agreement with the experiment (cf. Table 1)—diacetyl (K18) should not be enolic whereas in cyclopentane-1.2-dione (K20) and cyclohexane-1.2-dione (K21) the enol should be dominant. The relation between the ΔKE values of cyclopentane-1.2-dione (K20) and cyclohexane-1.2-dione (K21) is reverse to the corresponding ΔG values of Table 1. The same applies to the relation between the ΔKE values of cyclohexane-1.3-dione (K16) and cyclohexane-1.2-dione (K21).

A comparison between the experimental ΔG values and the *ab initio* calculated ΔKE values is given in Table 1. This comparison is disappointing because the differences $\Delta KE - \Delta G$ vary rather strongly. But note that only the value of acetylacetone is suitable for such a comparison because the experimental measurements of the other compounds are not performed in the gas phase. The average value for $\Delta KE - \Delta G$ is 10 kcal/mole. Large deviations of $\Delta KE - \Delta G$ from this value are obtained for cyclopentanone, acetylacetone and cyclohexane-1.2-dione.

7. Discussion of the Results

In this section conclusions are made from the data of the foregoing section by comparing the structure of the molecules with their ΔKE and their difference values (difference value = $B_{\text{calculated}} - B_{\text{estimated}}$). The observations, which can be made for all the compounds (groups *A-D*), are summarized in the following statements. Note that these statements are only valid in the context of the approximations inherent in the method of calculation.

7.1. Influence of the Chain Length

The alternance of ΔG , which was experimentally observed by Gero [2] in acyclic monoketones (cf. Table 1 and Sect. 2.4), is not observed here. This can be seen at the ΔKE values of the reactions $K4 \rightarrow E4a$ and $K5 \rightarrow E5a$ (see Fig. 1*a*) which are equal to each other. The negligible difference values $K4(K3)$ and $E5a(E4a)$ indicate that the linkage energy for lengthening the chain $K3 \rightarrow K4$ and $E4a \rightarrow E5a$ converges towards the value of $\Delta l = -0.378$ a.u., which is normal for alkanes (see linkage $L1$ and Δl of Table 2). Therefore one can expect with high probability that a further lengthening of the chains requires again the energy Δl for the keto form as well as for the enol form so that ΔKE will remain constant. (This is the reason why the binding energy of $K5$ is estimated from the known binding energy of $K4$ but not calculated.)

7.2. Stabilizing Influence of CH_3 or $-\text{CH}_2-$ Groups

From Table 2 one can see that the linkage L_3 of a CH_3 or CH_2 group to a $\text{C}=\text{C}$ double bond is favoured by 4.5 kcal/mole compared to the linkage L_1 of a CH_3

group to a C—C single bond. From experimental data one obtains for this stabilization energy 2.7 kcal/mole [12]. This effect is often called “hyperconjugation” and plays an important part in the keto–enol tautomerism. It can be easily observed at the ΔKE values of the Reactions 3–5 (cf. Fig. 1a) which are all lower by 3–5 kcal/mole than the ΔKE value of Reaction 2 (cf. Fig. 1a). This is in agreement with the experimental results of Table 1. The difference values (cf. Fig. 1a) of the molecules considered do not deviate strongly from zero. This means that the molecules of the Reactions 3–5 have no extraordinary properties with respect to the smaller molecules of Reaction 2 and with respect to the linkages L_1 and L_3 which are used for the energy estimation. Therefore one can state that the difference between the linkage energies $\Delta 1$ and $\Delta 3$ (cf. Table 2), or the hyperconjugation, respectively, must be responsible for the different ΔKE values of Reaction 2 and the Reactions 3–5.

The stabilizing influence of CH_3 — or — CH_2 — groups at the carbonyl double bond amounts to only $\Delta 2 - \Delta 1 \approx 2$ kcal/mole (cf. Table 2). If one calculates ΔKE of Reaction 1 with the enol E1a instead of E1b (because E1a has the same conformation as E2a) one can see from the ΔKE values of the Reactions 1–2 that the stabilization of the C=C double bond in E2a overcompensates the stabilization of the C=O group in K2.

The stabilization energy at the C=C double bond is raised by additional 1.5–2.5 kcal/mole to about 6 kcal/mole if the CH_3 — or the — CH_2 — group is linked to a system of conjugated double bonds. This can be observed at the difference values E11a(E10a) (cf. Fig. 1b) and E19a(E17a) (cf. Fig. 1d).

The hyperconjugation outlined here is responsible for the fact that the cyclic 1,2-diketones K20 and K21 (cf. Fig. 1d) are considerably more enolic than diacetyl (K18) (cf. Table 1 and Sect. 2.1). This is because the enols of the former have a — CH_2 — group adjacent to the C=C double bond whereas the enols of diacetyl do not have. The statement is supported by the result that the reaction of the acyclic 1,2-diketone K19 has roughly the same ΔKE value as the reactions of the cyclic 1,2-diketones.

In the literature the discrepancy between acyclic and cyclic 1,2-diketones is explained by the fact that the cyclic compounds are not able to have the more favourable *trans* arrangement whereas the acyclic compounds are able [9]. Moreover, entropy effects should favour the enolization of cyclic compounds compared to acyclic ones as it was already outlined in Sect. 2.2. However, the results just discussed here show that the hyperconjugation must at least be also responsible for the different ΔKE values of diacetyl (K18) and the cyclic 1,2-diketones.

7.3. Destabilizing Influence of CH_3 Groups

On the other hand the CH_3 group has a destabilizing influence in the systems *I* and *II* of Fig. 2. This can be observed at the positive difference values E2b(E1b), E11b(E10b) and E19b(E17b). E2b and E11b contain the system *I* and E19b the system *II*. The distance H1–H3 = H2–H3 (cf. Fig. 2) is larger than 2.4 Å in E2b and E11b and larger than 2 Å in E19b, so that steric interactions can be excluded.

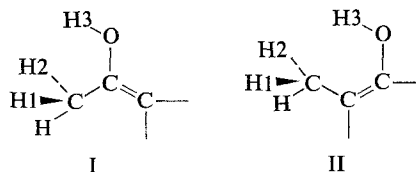


Fig. 2 The energetically unfavourable systems I and II

Perhaps this destabilization is caused by a repulsive interaction between the rather positive net charge of +0.23 at H3 and the weak positive net charge of +0.07 at H1 and H2. If one replaces these atoms by point charges containing the atomic net charges one obtains a repulsive energy of about 4.5 kcal/mole. Also in the compounds E14a and E14b (cf. Fig. 1c) the CH₃ group has a destabilizing influence as it can be observed at the positive difference values E14a(E13) and E14b(E13). An explanation for this result could not be found in this work.

7.4. Hydrogen Bonds in Enols of 1,3-Diketones

The energy E_H of the hydrogen bond in the enols of 1,3-diketones shall be defined here as follows: $E_{H1} = B(E10b) - B(E10a) = 4.4$ kcal/mole and $E_{H2} = B(E11b) - B(E11a) = 10$ kcal/mole (cf. Fig. 1b). From the difference values $E11a(E10a) = -1.9$ kcal/mole and $E11b(E10b) = +3.8$ kcal/mole one can conclude that the large value E_{H2} is not the consequence of a stronger hydrogen bond in E11a—in that case E11a(E10a) should be more negative—but is a consequence of the unfavourable compound E11b. This compound has a methyl group positioned at the chelate ring and thus belongs to the unfavourable form I of Fig. 2 which was already discussed in the foregoing section.

In the enols of acyclic 1,3-diketones the hydrogen bond has a large influence on the charge distribution of the system of conjugated double bonds. This can be illustrated at the overlap populations P_{ij} between atom i and atom j of E10a and E10b (the numbering of the atoms is given in Fig. 1b):

$$\begin{array}{llll} \text{E10a: } P_{21} = 0.594 & P_{32} = 1.156 & P_{43} = 0.838 & P_{54} = 0.811 \\ \text{E10b: } P_{21} = 0.581 & P_{32} = 1.177 & P_{43} = 0.829 & P_{54} = 0.821 \end{array}$$

This means that the formation of the hydrogen bond increases the overlap population of single bonds and reduces the overlap population of double bonds in E10a and E11a.

7.5. Hydrogen Bonds in Enols of 1,2-Diketones

In the enols of 1,2-diketones exists a hydrogen bond which is partly responsible for the large amount of enol in cyclic 1,2 diketones. The hydrogen bond energies defined as in Sect. 7.4 are: $E_{H3} = B(E17b) - B(E17a) = 3.8$ kcal/mole and $E_{H4} = B(E19b) - B(E19a) = 7.5$ kcal/mole (cf. Fig. 1d). The difference values $E19a(E17a) = -1.3$ kcal/mole and $E19b(E17b) = +2.5$ kcal/mole (cf. Fig. 1d) lead to an explanation similar to that of the foregoing section. E_{H4} is large because E19b is energetically unfavourable with its unfavourable system II of Fig. 2.

In contrast to the enols of 1.3-diketones the formation of the hydrogen bond in enols of 1.2-diketones has a negligible influence on the system of conjugated double bonds. This is in accordance with the rather small overlap population of the hydrogen bond which is 0.009 in E17a, E18 etc., whereas this value is 0.027 in the enols E10a and E11a of acyclic 1.3-diketones.

7.6. Influence of OH Groups

The two enols E13: HO—CH=CH—HC=O (cf. Fig. 1c) and E17b: H₂C=COH—HC=O (cf. Fig. 1d) do not have a hydrogen bond and are the most simple enolic representatives of 1.3- and 1.2-diketones. E13 is favoured by 5.6 kcal/mole compared to E17b. This is partly responsible for the result that the amount of enol in cyclic 1.3-diketones resembles that of cyclic 1.2 diketones, although the former cannot have a hydrogen bond whereas the latter have.

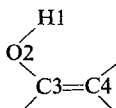
The overlap population of the C—C single bond between the two double bonds is 0.830 in E13 and 0.816 in E17b. This indicates that the position of the OH group in E13 favours the delocalization of the electron density compared to E17b.

7.7. Conjugated and Separated C=O Double Bonds

A system of two conjugated C=O double bonds is not favoured compared to a system with separated C=O double bonds. This can be seen at the roughly equal energies of the acyclic 1.3- and 1.2-diketones as K10, K11 on the one hand and K17, K18 on the other hand. The cyclic 1.2-diketones K20 and K21 are even strongly disfavoured compared to the corresponding 1.3 diketones K15 and K16.

7.8. Planarity of the System HO—C=C

In the system



the planar conformation is favoured by about 5 kcal/mole compared to that conformation where H1 looks out of the plane $P(O2, C3, C4)$ with the dihedral angle $\angle(H1, O2, C3, C4) = 90^\circ$. Regard the binding energies of the compounds E2a, E3a, E4a on the one hand and of E2c, E3c, E4c on the other hand. A further difference can be observed at the overlap population C3—O2 which is 0.573 in the planar and 0.541 in the nonplanar conformation.

7.9. Mutual Influence of Carbonyl and Hydroxyl Groups

C=O and O—H groups which are separated by more than one —CH₂— group can be considered as isolated from each other. This is supported by the difference values of K8, E8, K9 and E9 which are all near zero.

7.10. Exceptional Properties of 5-Ring Enols

Of special interest is one property which can be deduced from the difference values of 5-ring compounds with a C=C double bond. The angle at the —C=C— double bond will be denoted by α in the following discussion. As already outlined in Sect. 4, one has to start from *trans*-2-butene with $\alpha \approx 111^\circ$ in order to estimate the energy of cyclopentene. The energy of *trans*-2-butene is raised by ≈ 10 kcal/mole if α is reduced from 120° to $\approx 111^\circ$. Therefore one should expect the energies of 5-ring compounds with $\alpha \approx 111^\circ$ to be larger by about 10 kcal/mole than the energies estimated from analogous acyclic compounds with $\alpha = 120^\circ$ (no consideration of different angles). But they should be roughly equal to the energies estimated from acyclic compounds with $\alpha \approx 111^\circ$ (consideration of the different angles). However, the difference values of Fig. 1*a-d* indicate that the calculated energy of the 5-ring enols equals roughly the energy estimated from acyclic compounds with $\alpha = 120^\circ$ and is lower by about 15 kcal/mole than the value estimated from acyclic compounds with $\alpha \approx 111^\circ$! So one can state that the 5-ring enols are more stable by about 15 kcal/mole than one would expect if they would behave like acyclic compounds. To illustrate this statement the difference values of all calculated 5-ring compounds (cf. Fig. 1*a-d*) containing a C=C double bond shall be given here once more in kcal/mole (the estimation is performed with $\alpha = 120^\circ$ and $\alpha \approx 111^\circ$ in the acyclic compounds):

| | | |
|---------------------------------------|------------|-------------|
| cyclopentene(<i>trans</i> -2-butene) | 120°: -3.1 | 111°: -14.4 |
| E6(E3 <i>a</i>) | 120°: +4.4 | 111°: -6.9 |
| E15(E14 <i>b, d</i>) | 120°: -4.4 | 111°: -18.8 |
| E20(E19 <i>a</i>) | 120°: +0.6 | 111°: -16.3 |

An exception is the enol E6 of cyclopentanone, but nevertheless this molecule is still more stable by about 7 kcal/mole than one would expect from an estimation with $\alpha \approx 111^\circ$.

The exceptional behaviour of 5-ring compounds containing a C=C double bond is also observed at the overlap population P_{ij} in the system C1—C2=C3—C4 which is a part of the cyclic and acyclic enols. In acyclic compounds, as *trans*-2-butene or *trans*-3-hexene, P_{21} and P_{43} decrease if α is reduced from 120° to about 111° . In cyclopentene, however, with $\alpha \approx 111^\circ$, P_{21} and P_{43} are even larger than the corresponding populations of the acyclic compounds with $\alpha = 120^\circ$. This behaviour, which is similar to that of the binding energies and difference values, is illustrated in

Table 3. Overlap populations P_{ij} in the system

$$\begin{array}{c} \text{OH} \quad \text{H} \quad \text{O4} \\ | \quad | \quad || \\ \text{C}-\text{C1}=\text{C2}-\text{C3}- \end{array}$$
 which belongs to the enols of cyclic 1,3-diketones. For notation see Figs. 1*a-d*. $\alpha = \angle(\text{C}, \text{C1}, \text{C2}) \approx \angle(\text{C1}, \text{C2}, \text{C3})$. Remarkable is the exceptional behaviour of the five-ring enol E15

| Enol | α | P_{21} | P_{32} | P_{43} |
|--------------|----------|----------|----------|----------|
| E13 | 120 | 1.174 | 0.830 | 0.824 |
| E14 <i>a</i> | 120 | 1.176 | 0.834 | 0.822 |
| E14 <i>b</i> | 120 | 1.174 | 0.834 | 0.818 |
| E14 <i>d</i> | 111 | 1.172 | 0.825 | 0.818 |
| E15 | 111 | 1.166 | 0.845 | 0.810 |
| E16 | 123 | 1.181 | 0.838 | 0.817 |

| Enol | α | P_{12} | P_{32} | P_{43} |
|------|----------|----------|----------|----------|
| E17a | 120 | 1.189 | 0.812 | 0.819 |
| E18 | 120 | 1.190 | 0.816 | 0.814 |
| E19a | 120 | 1.194 | 0.816 | 0.817 |
| E19a | 111 | 1.185 | 0.809 | 0.813 |
| E20 | 111 | 1.184 | 0.825 | 0.805 |
| E21 | 123 | 1.200 | 0.820 | 0.814 |

Table 4. Overlap populations P_{ij} in the system

$$\begin{array}{c} \text{H} \quad \text{OH} \quad \text{O4} \\ | \quad || \quad || \\ \text{C}-\text{C1}=\text{C2}-\text{C3} \end{array}$$
 which belongs to the enols of cyclic 1,2-diketones. For notation see Figs. 1a-1d. $\alpha = \angle(\text{C}, \text{C1}, \text{C2}) \approx \angle(\text{C1}, \text{C2}, \text{C3})$. Remarkable is the exceptional behaviour of the five-ring enol E20

Tables 3-4 at the overlap population of the C—C single bond between the C=C and C=O double bond in enols of 1,2- and 1,3-diketones. Tables 3-4 show that the overlap population of the C=C and the C=O double bond is minimal in 5-ring enols, whereas the overlap population of the single bond between the two double bonds is maximal in 5-ring enols.

The results outlined in Sect. 7.10 are observed not only at the enols but also at cyclopentene, *trans*-2-butene and *trans*-3-hexene. Therefore it is reasonable to extend the statements to all 5-ring systems which contain a C=C double bond in the ring. If these results have a physical background and are not the consequence of the approximative nature of calculation, the same physical background should be responsible for the stability of cyclobutene and cyclopropene.

Appendix

The approximative HF method was developed in order to reduce the number of two-electron integrals which have to be evaluated. The method consists of the following concepts. The Coulomb and exchange parts of the HF matrix are treated differently with different integrals. In the Coulomb part the electron density P is subdivided into densities P_{aa} at an atom a and densities P_{ab} between atom a and atom b . Each partial density P_{ab} is approximated by only a few functions \tilde{P}_{ab} under the condition of charge conservation. It turned out that it was impossible to get satisfying results with only a small number of approximation functions which, however, is necessary in order to reduce the number of integrals considerably. To circumvent this difficulty, the densities \tilde{P}_{cd} are multiplied by a factor $Q_{cd(ij)}$, where i and j refer to the basis functions χ_i and χ_j in the Coulomb integrals:

$$J_{ij} = \int \chi_i(1)\chi_j(1)r_{12}^{-1}P_{cd}(2) d\tau_1 d\tau_2.$$

The factor causes the potential of the approximate density \tilde{P}_{cd} to resemble that of the "exact" density P_{cd} in that region, where $\chi_i\chi_j$ has large values.

The exchange part is treated in such a way that every function χ of the original basis set occurring in the exchange integrals is replaced by a function $\tilde{\chi}$ of an associated basis set which consist of fewer Gaussian lobes. In order to reduce the error caused by this procedure, the further replacement $\chi_i\chi_j \rightarrow Q_{ij}\tilde{\chi}_i\tilde{\chi}_j$ is performed, where Q_{ij} causes the charge and the Coulomb potential of $\chi_i\chi_j$ and $Q_{ij}\tilde{\chi}_i\tilde{\chi}_j$ to roughly coincide.

Two different levels of approximation are tested. At level **b** all one-centre two-electron integrals (over Gaussian lobes) and also all two-centre integrals between neighbouring H and first-row atoms—e.g. C—H but not C—C—are calculated exactly. The results of this work refer to this level. The computer time of the integral part for a molecule as CF_4 is reduced by a factor 6 compared to a normal HF program of comparable efficiency in the integral part for integrals over Gaussian lobes. The error in the energy is—compared to “exact” HF calculations—0.03–0.04 a.u. for molecules with 2–3 first-row atoms as acetaldehyde and about 0.08 a.u. for molecules as cyclopentene. The error in the reaction energies is about 5 kcal/mole if the number of bonds between first-row atoms is not changed by the reaction. This condition is satisfied here. At level **a** all two-centre integrals between neighbouring atoms are calculated exactly. The error in the energy is up to 0.025 a.u. for molecules which contain up to 6 first-row atoms as e.g. cyclopentanone. In the reaction energies the error is about 5 kcal/mole also for reactions where the number of bonds between first-row atoms is not conserved. In addition several calculations are performed at level **a** and lead to the same results as those of level **b**.

Acknowledgment. I would like to thank Prof. Dr. H. Preuss for continuously supporting this work.

References

1. Wheland, G. W.: Resonance in organic chemistry, pp. 401–413. New York: John Wiley & Sons 1955
2. Gero, A.: J. Org. Chem. **19**, 469, 1960 (1954)
3. Schwarzenbach, G., Felder, E.: Helv. Chim. Acta **27**, 1044 (1944)
4. Schwarzenbach, G., Wittwer, C.: Helv. Chim. Acta **30**, 669 (1947)
5. Schwarzenbach, G., Wittwer, C.: Helv. Chim. Acta **30**, 663 (1947)
6. Conant, J. B., Thompson, A. F.: J. Am. Chem. Soc. **54**, 4039 (1932)
7. Briegleb, G., Strohmeier, W.: Angew. Chem. **64**, 409 (1952)
8. Gould, E. S.: Mechanismus und Struktur in der organischen Chemie. Weinheim: Verlag Chemie 1962
9. Wheland, G. W.: J. Chem. Phys. **1**, 731 (1933)
10. Schwarzenbach, G., Zimmermann, M., Prelog, V.: Helv. Chim. Acta **34**, 1954 (1951)
11. Strohmeier, W., Höhne, I.: Z. Naturforsch. **8b**, 53 (1953)
12. Roberts, J. D., Caserio, M. C.: Basic principles of organic chemistry, p. 174. New York–Amsterdam: W. A. Benjamin 1965
13. Hehre, W. H., Stewart, R. F., Pople, J. A.: J. Chem. Phys. **51**, 2657 (1969)
14. Pople, J. A., Gordon, M.: J. Am. Chem. Soc. **89**, 4253 (1967)
15. Stoll, H.: Theoret. Chim. Acta (Berl.) **49**, 143 (1978)
16. Kilb, R. W., Lin, C. C., Wilson, E. B.: J. Chem. Phys. **26**, 1695 (1957)

Received August 9, 1978/February 20, 1979