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Large structural effects in neutral and protonated species: a computational study[†]

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ABSTRACT: The B3LYP/6-31G(d) methodology was applied to the study of the diketone pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione (**1**), the hydrocarbon pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (**2**) and the ketone pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8-one (**3**). Also examined were the oxygen-protonated species **1**H^+ and **3**H^+. The diketone pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-4,8-dione (**4**) and the ketone pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-4-one (**5**) and their protonated forms were used for comparison purposes. This information was used to construct several isodesmic reactions, allowing the quantitative estimate of the influence of the carbonyl groups on the stability of the various species in the gas phase. These results were in excellent agreement with the experimental thermochemical and structural data available. Analyses by means of the natural bond orbital theory and simple electrostatic models were also performed. Copyright © 2001 John Wiley & Sons, Ltd.

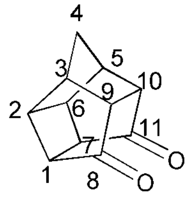
KEYWORDS: DFT; NBO; field/inductive effects; thermochemistry; proton affinities; strain

INTRODUCTION

Our interest in pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione (**1**) originates in a remarkable feature of its rigid structure, namely the presence of two carbonyl groups held at short distance in formally parallel planes.[1] Sizeable electrostatic interactions have been attributed[2,3] to this structural constraint.

From this point of view, oxygen protonation of **1** in the gas phase is also expected to lead to species affected by significant electrostatic effects.

This work initially addressed the problem of the quantitative estimate of these interactions in both the neutral and the protonated forms of **1**. The parent hydrocarbon, pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (**2**) and monoketone **3**, pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$] undecane-8-one were used as appropriate reference compounds. The study was later extended to the diketone **4**, pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-4,8-dione, using as references compounds **2, 3** and **5**, pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-4-one. We hoped that this information would be useful for the study of field/inductive effects.[4–9]



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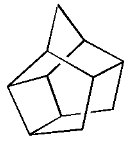

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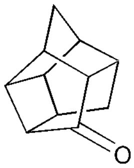

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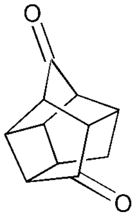

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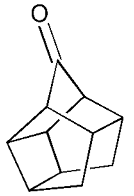

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The results of experimental and computational studies are reported below. Our approach is based on the determination of the standard enthalpy changes for isodesmic processes, such as the reaction in Eqn. (1), in the gas phase.

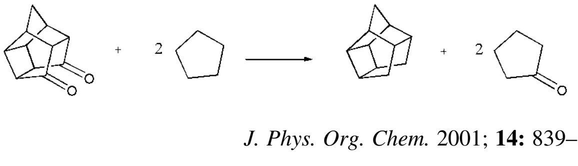

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Table 1. Experimental and computational energetic data for the relevant neutral and charged species

Species	$E^{a,b}$	ZPE^{a,c}	TCE^{a,d}	$H_{298}{}^{a,e,f}$	$\Delta_f H_m^0(g)^g$
1	−575.588 353	0.188 232	0.197 166	−575.394 839	−113.6 ± 3.4
2	−427.571 882	0.227 065	0.234 280	−427.342 007	71.7 ± 0.5
3	−501.583 217	0.207 722	0.215 793	−501.371 454	
4	−575.589 566 8	0.188 367	0.197 266	−575.395 955	
5	−501.580 069 3	0.207 890	0.215 918	−501.368 183	
1H^+	−575.917 848	0.200 292	0.209 573	−575.712 161	
3H^+	−501.926 217 6	0.220 034	0.228 422	−501.702 065	
4$H^+_{C(4)}$	−575.915 279 8	0.200 677	0.209 865	−575.709 308	
4$H^+_{C(4)}$	−575.920 066 5	0.200 381	0.209 617	−575.714 336	
5H^+	−501.917 647 9	0.220 309	0.228 659	−501.693 263	
c-C_5H_{10}	−196.557 025	0.141 457	0.147 557	−196.412 212	−76.8 ± 0.5
c-C_5H_8O	−270.572 823	0.121 933	0.128 413	−270.446 776	−46.6 ± 0.5
c-$C_5H_8OH^+$	−270.901 040 2	0.134 041	0.140 688	−270.762 953	

[a] Computed at the B3LYP/6-31G(d) level. All results in hartrees.

[b] Electronic and nuclear energies.

[c] Zero-point energy.

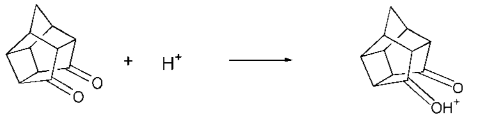
[d] Thermal correction to enthalpy.

[e] Corrected as indicated in the text.

[f] Defined as: $H_{298} = E + \text{ZPE(corrected)} + (\text{TCE} - \text{ZPE})$.

[g] Experimental values (kJ mol^{-1}) from Refs 1, 10 and 16.

Reactions of this kind provide simple models allowing the estimate of changes in energies (or enthalpies) associated with intramolecular interactions. For instance, $\Delta_r H^0(1)$ can be taken as a quantitative measure of the enhanced strain in **1** relative to that in the parent hydrocarbon; $\Delta_r H^0(1)$ can also be compared with other estimates of differences in strain and provides a lower limit for the destabilizing effect of the simultaneous presence of the two carbonyls. Both experimental and computational data can be used for the purpose of determining these reaction enthalpies.



(2)

Experimental enthalpies of formation for **1** and **2** are available, from Refs 1 and 10 respectively. We have also tried to use Fourier transform ion cyclotron resonance spectroscopy for the experimental determination of $\Delta_r G^0(2)$, the standard Gibbs energy change for the protonation of **1** in the gas phase, reaction (2). Unfortunately, we did not succeed, because of the very low vapor pressure of this compound.

In this work we combine the available experimental data with the results of computational studies.

COMPUTATIONAL RESULTS

The size of the various relevant species is such that very high computational levels were beyond our capabilities. We have chosen the density functional theory with the B3LYP functional[11,12] and the 6-31G(d) basis set[13] as a reasonable compromise between accuracy and computational effort. In all cases, geometries were fully optimized and analytical vibrational frequencies computed. Zero-point energies were corrected according to Scott and Radom.[14] Calculations were performed using the Gaussian 98 package of computer programs.[15] Results are presented in Table 1 together with the experimental information available.[1,10,16].

A natural bond orbital (NBO) analysis[17] was carried out to explore the orbital interactions in the species studied. The results are summarized in Table 2.

DISCUSSION

Structural results

The optimized structures of the various relevant species are summarized in Figs 1–5. The structures of **1**H^+, **3**H^+ and **4**H^+ presented in the figures have the hydrogen atoms of the hydroxyl group pointing towards C(1). Similar structures with the opposite orientation of the hydroxyl group were also found to be minima on the corresponding potential energy surfaces, but they are slightly less stable (about 0.4 kJ mol^{-1}).

All these structures share a common feature: the substantial distortion of the hydrocarbon 'cage'.

(1) In the case of the three neutrals, the C(2)—C(6) and C(8)—C(11) distances respectively remain in the

Table 2. NBO analysis of the bond–antibond orbital interaction energy

System	Orbital interactions[a]	Energy (kJ mol^{-1})
1	LP O(8)//BD* C(1)—C(8)	96.3
1	LP O(8)//BD* C(8)—C(9)	96.1
1	LP O(11)//BD* C(7)—C(11)	96.3
1	LP O(11)//BD* C(11)—C(10)	96.1
1H$^+$	LP O(8)//BD* C(1)—C(8)	38.5
1H$^+$	BD O(8)—H//BD* C(8)—C(9)	26.3
1H$^+$	LP O(11)//BD* C(7)—C(11)	104.9
1H$^+$	LP O(11)//BD* C(10)—C(11)	102.2
1H$^+$	BD C(1)—C(7)//BD* C(8)—O(8)	42.1
1H$^+$	BD C(9)—C(10)//BD* C(8)—O(8)	35.4
3	LP O(8)//BD* C(1)—C(8)	93.8
3	LP O(8)//BD* C(8)—C(9)	93.5
3H$^+$	LP O(8)//BD* C(1)—C(8)	37.2
3H$^+$	BD O(8)—H//BD* C(8)—C(9)	26.0
3H$^+$	BD C(1)—C(7)//BD* C(8)—O(8)	49.7
3H$^+$	BD C(9)—C(10)//BD* C(8)—O(8)	38.1
4	LP O(8)//BD* C(1)—C(8)	94.3
4	LP O(8)//BD* C(8)—C(9)	96.3
4	LP O(4)//BD* C(3)—C(4)	100.4
4	LP O(4)//BD* C(4)—C(5)	99.2
4H$^+$ (C4)	LP O(8)//BD* C(1)—C(8)	94.9
4H$^+$ (C4)	LP O(8)//BD C(8)—C(9)	110.1
4H$^+$ (C4)	BD O(4)—H//BD C(3)—C(4)	28.0
4H$^+$ (C4)	LP O(4)//BD*(1) C(4)—C(5)	40.4
4H$^+$ (C4)	BD C(5)—C(6)//BD* C(4)—O(4)	26.7
4H$^+$ (C4)	BD C(5)—C(10)//BD* C(4)—O(4)	30.7
4H$^+$ (C4)	BD C(2)—C(3)//BD C(4)—O(4)	25.2
4H$^+$ (C4)	BD C(3)—C(9)//BD* C(4)—O(4)	34.0
4H$^+$ (C8)	LP O(4)//BD* C(1)—C(8)	37.9
4H$^+$ (C8)	BD O(4)—H//BD* C(8)—C(9)	26.3
4H$^+$ (C8)	LP O(4)//BD* C(4)—C(5)	103.0
4H$^+$ (C8)	LP O(4)//BD* C(3)—C(4)	113.2
4H$^+$ (C8)	BD C(1)—C(7)//BD* C(8)—O(8)	45.4
4H$^+$ (C8)	BD C(9)—C(10)//BD* C(8)—O(8)	33.1
4H$^+$ (C8)	BD C(1)—C(2)//BD* C(8)—O(8)	25.4
4H$^+$ (C8)	BD C(3)—C(9)//BD* C(8)—O(8)	22.5
5	LP O(4)//BD* C(3)—C(4)	97.9
5	LP O(4)//BD* C(3)—C(5)	102.1
5H$^+$	LP O(4)//BD* C(3)—C(4)	39.6
5H$^+$	BD O(4)—H//BD* C(3)—C(5)	27.9
5H$^+$	BD C(2)—C(3)//BD* O(4)—C(4)	28.8
5H$^+$	BD C(9)—C(3)//BD* O(4)—C(4)	31.6
5H$^+$	BD C(6)—C(5)//BD* O(4)—C(4)	29.1
5H$^+$	BD C(5)—C(10)//BD* O(4)—C(4)	31.8

[a] LP: lone pair; BD: bonding; BD*: anti-bonding.

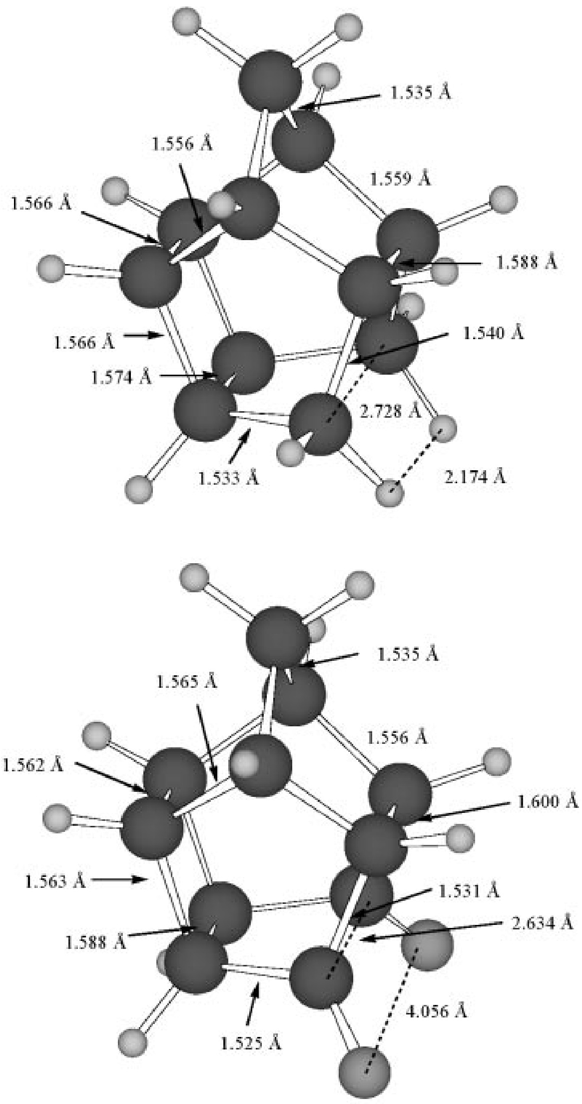


Figure 1. B3LYP/6-31G(d)-optimized structures of molecules **1** and **2**

ranges 1.56–1.57 Å and 2.63–2.73 Å. The computed O—O distance and the angle between the two carbonyl groups in **1** reach 4.06 Å and 72° respectively. Our results can be compared with the experimental X-ray structure of the 3-methyl derivative of **1**.[16] The agreement is very good (the average unsigned differences in bond lengths is *ca* 0.007 Å).

(2) In the case of the protonated species, the following facts are observed.

(a) In the cases of **1** and **3**, protonation of the carbonyl group produces a significant shortening (up to 0.06 Å) of the C—C bond attached to this group [C(1)—C(8) or C(8)—C(9)]. The NBO analysis (Table 2) shows that the interaction between the oxygen's lone pair with the corresponding antibonding C—C orbitals decreases when the former becomes protonated. The stabilization energy associated with the orbital interactions falls from a value of approximately 96 kJ mol^{-1} in the neutral species to 25–38 kJ mol^{-1} in the protonated forms.

(b) In the cases of **1** and **3**, a lengthening of up to 0.03 Å of two C—C bonds in β position relative to the carbonyl group is observed [C(9)—C(10) and C(1)—C(7)]. The interaction of these bonds with the carbonyl anti-bonding orbital in the protonated species (Table 2) explains the lengthening men-

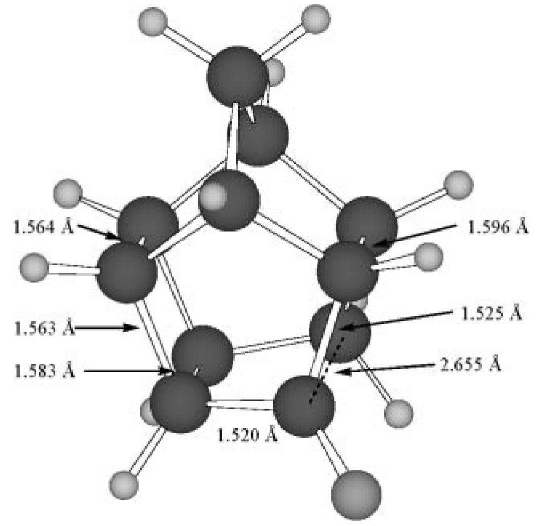


Figure 2. B3LYP/6-31G(d)-optimized structure of molecule **3**

tioned. Something similar has been found for other carbocations.[18]

(c) In the cases of **4** and **5**, protonation of the carbonyl group produces a shortening of the C—C bond in α position to this group (up to 0.06 Å) and a lengthening of those in β position (up to 0.04 Å). The NBO analysis of the bonding–antibonding interactions shows a smaller interaction between the lone pair of the carbonyl group and the antibonding C—C in α position when the former is protonated, and a larger one between the β C—C bonding orbital and the antibonding C—O.

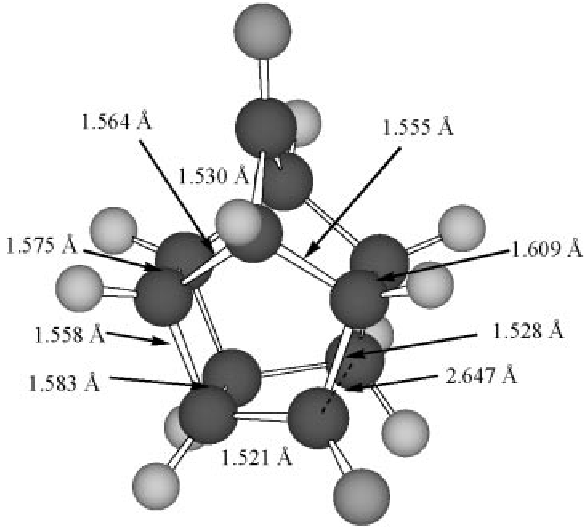


Figure 4. B3LYP/6-31G(d)-optimized structures of molecule **4**

(d) The OH group in $\mathbf{1}H^+$ is not oriented towards the neutral carbonyl group and no chelation occurs.

Energetic results

The experimental and computational data available have been used to examine the following processes in the case of molecules **1** and **3**:

(1) The stepwise substitution of the two carbonyl groups in **1** by two methylene groups, reactions (1) and (3);

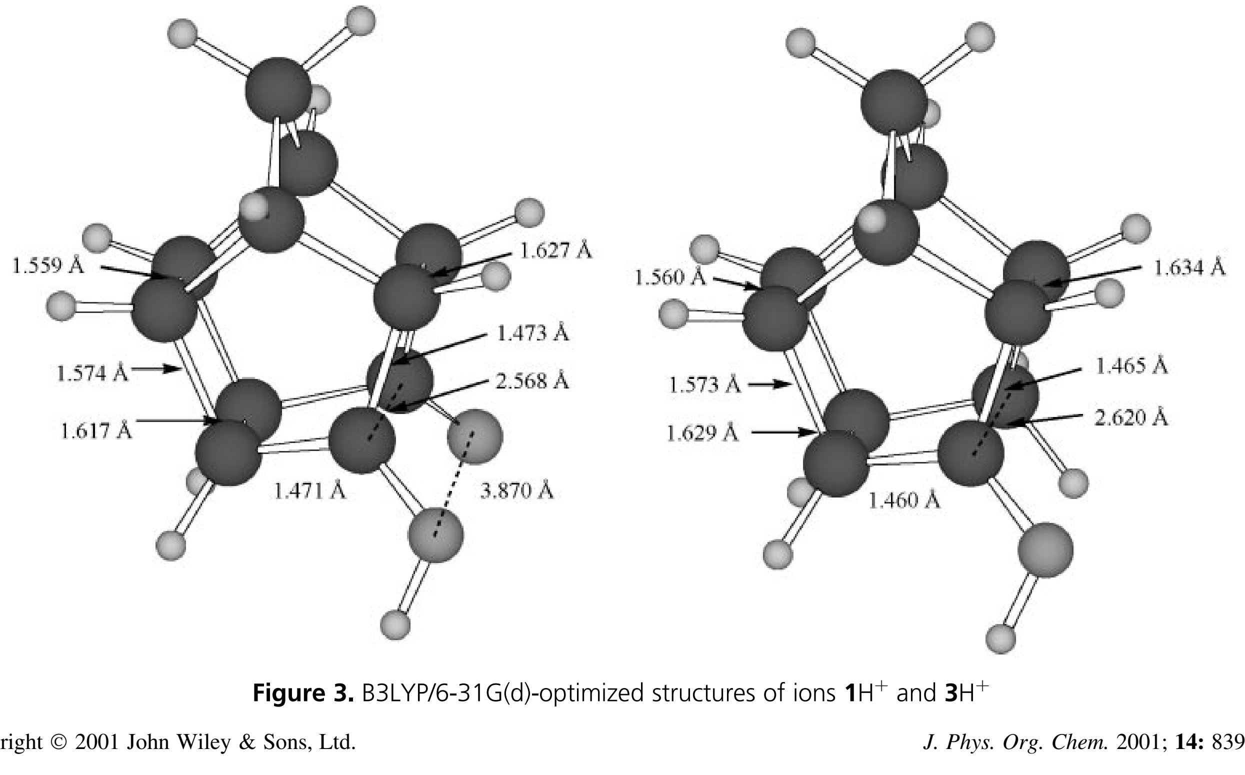


Figure 3. B3LYP/6-31G(d)-optimized structures of ions $\mathbf{1}H^+$ and $\mathbf{3}H^+$

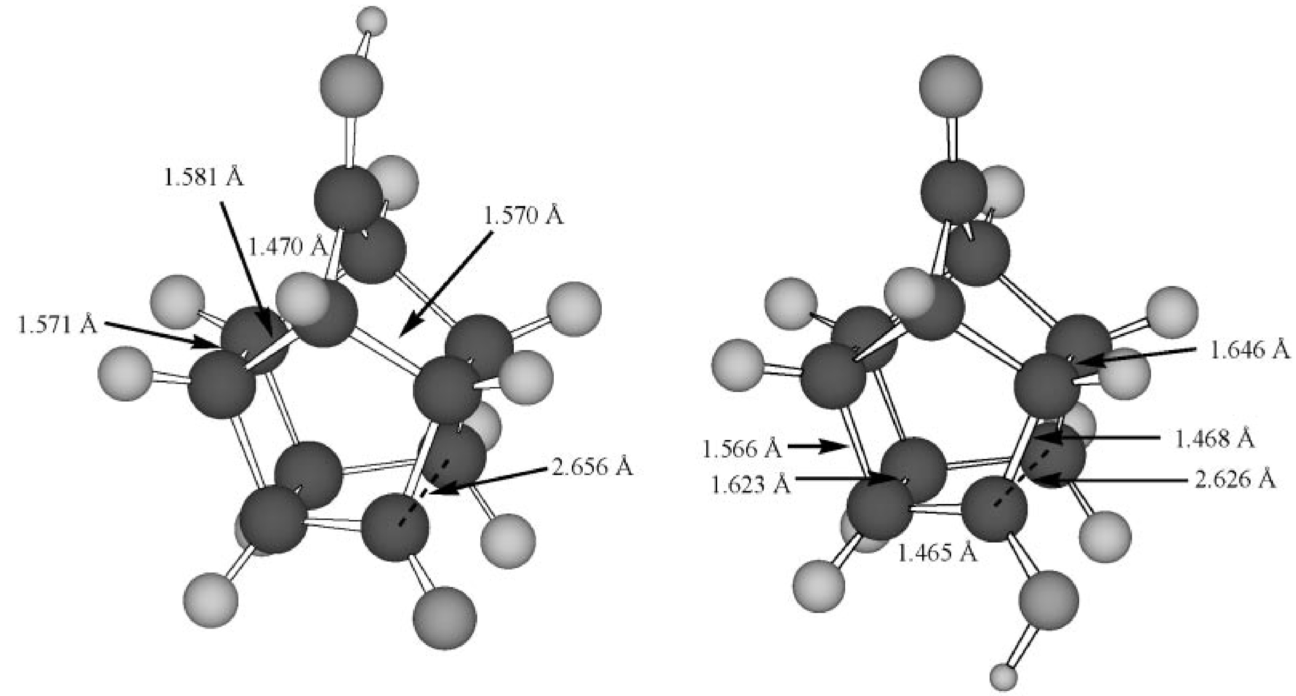
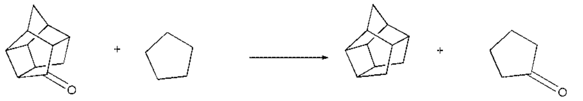


Figure 5. B3LYP/6-31G(d)-optimized structures of the isomeric species for **4**H^+(C4) and **4**H^+(C8)

(2) The proton exchange between **1** or **3**, and cyclopentanone, reactions (4) and (5);

(3) The stepwise substitution of the carbonyl groups in **1**H^+ by methylene groups, reactions (6) and (7).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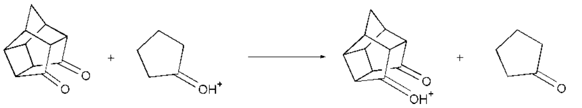
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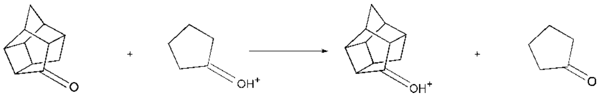
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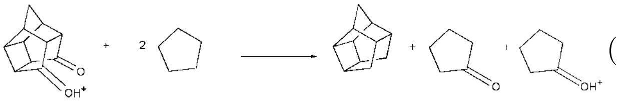
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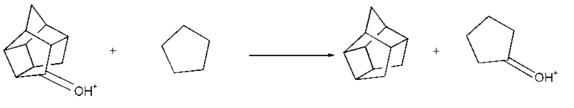
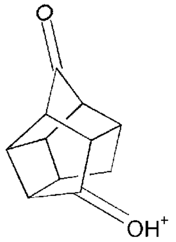
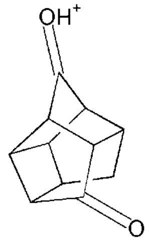

(7)

Similar reactions were examined in the cases of **4** and **5**. Notice that in the case of **4**, two different protonated forms exist:


4H^+(C8)


4H^+(C4)

$$\mathbf{4} + 2c\text{-}C_5H_{10} \rightarrow \mathbf{2} + 2c\text{-}C_5H_8O \quad (8)$$

$$\mathbf{5} + c\text{-}C_5H_{10} \rightarrow \mathbf{2} + c\text{-}C_5H_8O \quad (9)$$

$$\mathbf{4} + c\text{-}C_5H_8OH^+ \rightarrow \mathbf{4}H^+(C4) + c\text{-}C_5H_8O \quad (10a)$$

$$\mathbf{4} + c\text{-}C_5H_8OH^+ \rightarrow \mathbf{4}H^+(C8) + c\text{-}C_5H_8O \quad (10b)$$

$$\mathbf{5} + c\text{-}C_5H_8OH^+ \rightarrow \mathbf{5}H^+ + c\text{-}C_5H_8O \quad (11)$$

$$\mathbf{4}H^+(C4) + 2c\text{-}C_5H_{10} \rightarrow \mathbf{2} + c\text{-}C_5H_8OH^+ + c\text{-}C_5H_8O \quad (12a)$$

$$\mathbf{4}H^+(C8) + 2c\text{-}C_5H_{10} \rightarrow \mathbf{2} + c\text{-}C_5H_8OH^+ + c\text{-}C_5H_8O \quad (12b)$$

$$\mathbf{5}H^+ + c\text{-}C_5H_{10} \rightarrow \mathbf{2} + c\text{-}C_5H_8OH^+ \quad (13)$$

The standard enthalpy changes for these reactions are collected in Table 3.

Table 3. Standard enthalpy changes for selected isodesmic processes[a]

Reaction	$\Delta_r H^0_m(g)$(kJ mol^{-1})
1	−42.7,[a] −51.1 ± 4.1[b]
3	−13.3[a]
4	−2.9[a]
5	−38.1[a]
6	−39.8[a]
7	−24.5[a]
8	−39.9[a]
9	−22.0[a]
10a	7.4[a]
10b	−5.8[a]
11	−23.4[a]
12a	−47.3[a]
12b	−34.1[a]
13	1.4[a]

[a] Purely theoretical quantum mechanical value.
[b] Purely experimental value.

From these data we draw the following conclusions.

(1) $\Delta_r H^0_m$ for reaction (1) provides an estimate of the overall destabilizing effect of the two carbonyls in **1**, relative to **2**. The purely computational value of $\Delta_r H^0_m(1)$ amounts to −42.7 kJ mol^{-1}, in very good agreement with the purely experimental result (−51.1 ± 6.5 kJ mol^{-1}) obtained from data given in Table 1. Furthermore, two alternative ways were used to estimate the difference in strains between **1** and **2**: (i) Benson's additive scheme[19] was applied to both compounds in order to estimate $\Delta_f H^0_m(\mathbf{1})$ and $\Delta_f H^0_m(\mathbf{2})$ in the absence of strain. The resulting values are respectively −343.6 kJ mol^{-1} and −125.5 kJ mol^{-1}. When compared with experimental data, they were found to differ by 230.0 kJ mol^{-1} and 197.2 kJ mol^{-1} respectively. These differences can be taken as measures of strain effects in **1** and **2**. The difference between these strains thus equals 32.8 kJ mol^{-1}, in very fair agreement with the experimental value of $\Delta_r H^0_m(1)$. (ii) Similarly, Ibrahim's bond separation scheme[20] was applied to estimate strain-free enthalpies of formation for **1** and **2**. By following a procedure similar to that described above, the difference in strains between **1** and **2** is calculated as 39.4 kJ mol^{-1}. The agreement with the experimental value of $\Delta_r H^0_m(\mathbf{1})$ is excellent.

With respect to **4**, $\Delta_r H^0_m(8)$ has the same meaning as $\Delta_r H^0_m(1)$ relative to **1**. Their values are extremely close. Obviously, calculations of strain according to Benson[19] and Ibrahim[20] lead to very similar results.

(2) $\Delta_r H^0_m(3)$ is less than 30% of $\Delta_r H^0_m(1)$ and $\Delta_r H^0_m(9)$ is over 50% of $\Delta_r H^0_m(8)$. This indicates that the strain in the monoketone **5** is larger than in **3**. This is confirmed by the fact that the position of the computed C═O stretching vibration of the carbonyl group in **3** is very close to that for cyclopentanone, whereas that for **5** is 20 cm^{-1} higher.[21] The introduction of the second carbonyl enhances the strain, the effect being somewhat larger in the case of **1**. In the case of **4**, the destabilizing effects of the carbonyl groups are nearly additive, i.e. $\Delta_r H^0_m(8) \approx \Delta_r H^0_m(3) + \Delta_r H^0_m(9)$, whereas in the case of **1** they are significantly larger (in absolute value) than expected on the basis of additivity $[\Delta_r H^0_m(1) < 2\ \Delta_r H^0_m(3)]$. This indicates some degree of cooperativity in the destabilization of **1**.

(3) The proton affinity (PA) of a molecule is defined as the negative of its standard enthalpy of protonation.[22] For example, $\mathrm{PA}(\mathbf{1}) = -\Delta_r H^0_m(2)$. $\Delta_r H^0_m(4)$ is thus given by the difference between the PA of **1** and cyclopentanone. The fact that this reaction is practically thermoneutral is deceptively simple. The proton exchange between **3** and the latter, reaction (5), is seen to be exothermic by 38.1 kJ mol^{-1}. Thus, if we consider **1** and **3** as 'substituted cyclopentanones', it is clear that substitution of hydrogen atoms by the cyclopentane framework enhances the PA by some 38.1 kJ mol^{-1} and that substitution by a neutral cyclopentanone framework essentially offsets this stabilizing effect. This can be rationalized on the basis of stabilizing orbital interactions reported above or in terms of polarizability effects according to the Taft–Topsom model.[6] As regards diketone **4**, the pattern is similar. Thus, depending on the protonation site, the corresponding reaction enthalpies, $\Delta_r H^0_m(10a)$ and $\Delta_r H^0_m(10b)$ are again small in absolute value. $\Delta_r H^0_m(11)$, however, is also substantially negative.

Combination of $\Delta_r H^0_m(4)$ and $\Delta_r H^0_m(10b)$ provides $\Delta_r H^0_m(14)$, the standard enthalpy change for the process in Eqn. (14):

$$\mathbf{4}\mathrm{H}^+(\mathrm{C8}) + \mathbf{1} \rightarrow \mathbf{4} + \mathbf{1}\mathrm{H}^+ \qquad (14)$$

We find that $\Delta_r H^0_m(14) = 2.9$ kJ mol^{-1}. *The important implication of this result is that carbonyl groups in positions 4 and 11 exert essentially the same effect on the stability of the protonated species.*

On a semi-quantitative basis, the structural effects on the stabilities of the neutral species seem in line with the results to be expected on the basis of classical electrostatic models for substituent effects.[4–9] One of the simplest electrostatic models assumes that the two carbonyl groups in **1** act as ideal dipoles located at the mid-points of the C═O bonds. Using the structural data obtained from the present study, and considering that the overall dipole moment of **1**, 5.03 D, is the vectorial sum of the bond moments of the carbonyl groups, a positive (repulsive) carbonyl–carbonyl interaction energy[23] of 20.5 kJ mol^{-1} is obtained. If the carbonyl groups remained parallel, and at the same distance, the repulsion would reach 31.5 kJ mol^{-1}. These are values of the order of magnitude of the observed effects. Because of the larger separation between the carbonyl groups in **4**, the repulsive effect is expected to be appreciably smaller, as indeed is the case. On the other hand, consideration of $\Delta_r H_m^0(14)$ shows that the simple model is no longer valid in the case of the protonated species. In fact, one would expect an even larger destabilizing effect in **1**H$^+$ than in **1** (charge–dipole interactions instead of dipole–dipole). Actually, the opposite behavior is found [compare results for reactions (1) and (6)].

The quantum-mechanical calculations reported above rationalize these results. Protonation in any position induces significant structural changes. Furthermore, as NBO calculations indicate, orbital interactions are quite important and account for the structural modifications. Interestingly, orbital interactions are also significant in the neutral species. It is then fair to ask whether the reasonable conclusions of the classical model in the case of the neutral species are simply fortuitous. We have no answer to this question at this point.

The theoretical calculations used above are able to reproduce satisfactorily the available experimental data. They also provided useful insights into the structural effects of the carbonyl groups, both neutral and protonated. We are well aware of the fact that we are moving against a background of over 60 years of intensive study of these interactions, also known as field/inductive effects.[4–9] We do not intend by any means to contribute any mechanistic hypothesis, particularly as regards the through-bond/through-space mechanism of transmission of effects. We were guided in this study by the very simple concept that effects are large if the distances between the relevant dipoles are small. This was confirmed in the case of the neutral species, although this result was achieved at the cost of increasing the rigidity of the molecular framework through an increase in the number of connecting bonds. Formally, these results are qualitatively consistent with current concepts on field/inductive effects. On the other hand, the simple electrostatic model seems to fail in the case of the protonated species, possibly because of the very large structural changes induced by protonation. Obviously, this detracts in no way from the extraordinary qualitative and quantitative usefulness of field/inductive parameters for heuristic and predictive purposes in correlation studies in which these large structural changes are absent.

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