CROATICA CHEMICA ACTA
CCACAA, ISSN-0011-1643, ISSN-1334-417X
Croat. Chem. Acta **82** (1) (2009) 71-77.
CCA-3297

Original Scientific Paper

Proton and Lithium Cation Binding to Some β-Dicarbonyl Compounds. A Theoretical Study*

Peeter Burk, ** **Kristo Taul, and Jaana Tammiku-Taul**

Institute of Chemistry, Tartu University, 2 Jakobi St., Tartu, 51014, Estonia

RECEIVED JUNE 2, 2008; REVISED SEPTEMBER 26, 2008; ACCEPTED SEPTEMBER 30, 2008

Abstract. DFT B3LYP/6-311+G** calculations were performed to study the proton and lithium cation binding to the acetylacetone, hexafluoroacetylacetone, diacetamide, and hexafluorodiacetamide. It was shown that the most stable Li^+ adduct always corresponds to cyclic complex based on the *trans, trans*-keto form of the base. The product of protonation was found to be similar *trans, trans*-keto form based cyclic structure in case of diacetamide and hexafluorodiacetamide, while for acetylacetone and hexafluoroacetylacetone the protonation simply involves the addition of proton to (free) carbonyl oxygen in already cyclic enol form of the base with possible rotation of O–H bond.

Keywords: keto-enol tautomerism, proton affinity, lithium cation afifinity, DFT calculations

INTRODUCTION

The two Lewis acids H^+ and Li^+ present a significant contrast in the nature of the bond formed with the ligand.[1–8] The proton adds to the base giving a polar covalent sigma bond with a very extensive charge transfer (the positive charge on the hydrogen atom is usually 0.4 or less electronic units whereas the base molecule carries the rest of the positive charge). The large degree of charge transfer results from the fact that H^+ is a bare nucleus, with a very low energy unfilled 1s orbital. On the contrary, the bond formed by Li^+ (with its filled 1s shell) and other alkali metal cations is largely ionic (*i.e.* electrostatic ion-dipole, ion-induced dipole, *etc.* interaction) and the alkali metal cation retains 0.8 to 0.9 units of the positive charge in the complex.[1–8]

As a result, the gas-phase lithium cation affinities (LCAs) or lithium cation basicities (LCBs) are much smaller than proton affinities (PAs) or gas-phase basicities (towards proton, GBs), and cover much narrower range in the energy scale.[1,4] The widely different bonding types in H^+ and Li^+ adducts should lead to widely varying basicity orders.[8–11]

Earlier comparisons[10,11] of experimental basicities toward H^+ and Li^+ have led to the conclusion that there is no precise general correlation between LCBs and GBs, especially when diverse families of compounds with different functional groups are included, while satisfactory correlations were found for families with the similar basicity center. The lack of overall correlation is attributed[11] to the widely variable sensitivities in different series to the changes in substituents, as well as to some special effects like chelation in some Li^+ adducts or different basicity centers for proton and lithium cation.

The assumption that proton and Li^+ bind to different basicity centers was used to rationalize the deviations of several formally β-dicarbonyl compounds from otherwise reasonable correlation between PA-s and LCA-s.[11] In fact, it is well established that both acetylacetone and hexafluoroacetylacetone adopt hydrogen bonded enol structure in their most stable conformation.[12–17] It was proposed that lithium cation binding to β-dicarbonyl compounds predominantly occurs at carbonyl oxygen, and the replaced O–H hydrogen will migrate to the position it holds in ketone form (carbon or nitrogen, see Figure 1). This hypothesis was supported by DFT calculations on some conformers for both protonated and lithiated bases.

We report a complete DFT investigation of all conformations of protonation and lithium cation addition sites of several β-dicarbonyl compounds: acetylacetone (ACAC), hexafluoroacetylacetone (HFAA), diacetamide (DIAC), and hexafluorodiacetamide (HFDAC) in a current paper.

---

* Dedicated to Professor Zvonimir Maksić on the occasion of his 70th birthday.

** Author to whom correspondence should be addressed. (E-mail: peeter.burk@ut.ee)

METHODS

Standard density functional calculations using B3LYP hybrid method with 6-311+G** basis set were performed using the Gaussian 03 program package.[21]

As shown in Figure 2, different conformations of the keto and enol forms of studied neutral β-dicarbonyl compounds can be generated by rotating the two RC(O)− groups around RC(O)−C or RC(O)−N bonds while for the enol forms additional conformers can be obtained by rotating the O−H group around C−O bond. Considering *trans*- and *cis*-conformations around each of these bonds allows three conformers for keto form and eight conformers for enol form. All possible conformers of neutral, protonated, and lithiated molecules were fully optimized and the frequencies were calculated at B3LYP/6-311+G** levels. No scaling was applied to obtained DFT frequencies for the calculation of thermodynamic parameters (at 298.15 K) using standard procedures.[22] Total energies, enthalpies, and Gibbs free energies for most important structures are given in Tables 1−3. All energies and structures are available from authors upon request. In further discussions we have used enthalpies (at 298.15 K) for comparing the stabilities of different conformers.

Gas-phase proton and lithium cation basicities were obtained from calculated free energies (*G*, at 298 K) as defined by formulas (1) and (2) and are given in Table 4. Basis set superposition error was considered to be small and no correction was applied.

$$\mathrm{GB} = G_{\mathrm{H}^+} + G_{\mathrm{B}} - G_{[\mathrm{BH}]^+} \quad (1)$$

$$\mathrm{LCB} = G_{\mathrm{Li}^+} + G_{\mathrm{B}} - G_{[\mathrm{BLi}]^+} \quad (2)$$

Calculated gas-phase basicities are in a good correspondence (see Table 4) with experimental ones[23,24] (differences are 0.7, 2.6, and 4.5 kcal mol^{-1} for ACAC, HFAA, and HFDAC, respectively, 1 kcal mol^{-1} = 4.184 kJ mol^{-1}) and confirm the ability of chosen method to predict the proton basicities with high accuracy.[25] Lithium cation basicities are somewhat overestimated (by 9.5, 3.2, and 4.3 kcal mol^{-1} for ACAC, HFAA, and HFDAC, respectively) by the used method as we have noted earlier.[11] This overestimation is especially pronounced for bases with experimental lithium cation basicities over 36 kcal mol^{-1} (*i.e.* ACAC). We have shown that for high LCB values there exists a big difference between calculated and experimental results (at W1 level,[26] which should yield energies within 0.3 kcal mol^{-1} accuracy,[27] the difference between calculated and experimentally reported LCB is 8.1 kcal mol^{-1} (Ref. 28)). The origin of such a big discrepancy needs further exploration.

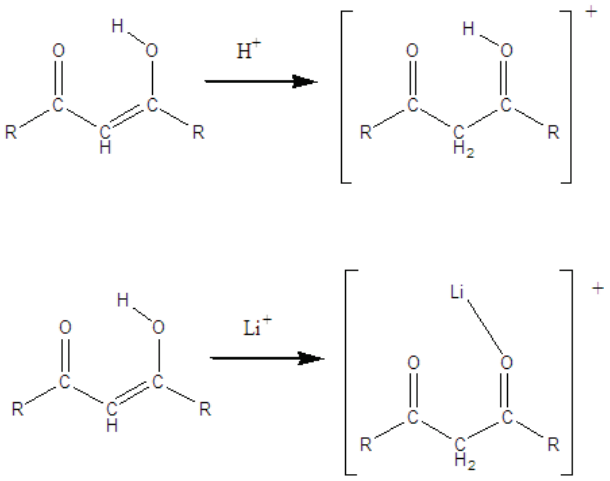

Figure 1. Proposed different mechanisms for proton and lithium cation addition to β-dicarbonyl compounds.[11]

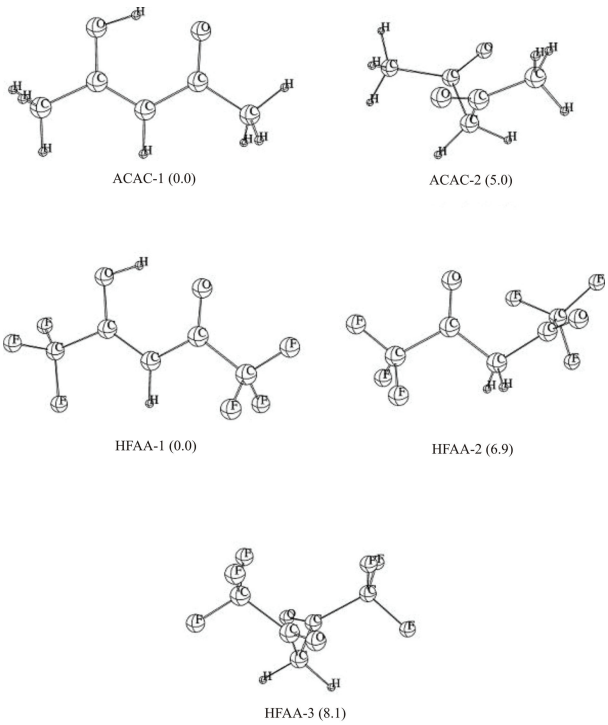

Figure 2. The most stable conformations of ACAC and HFAA. The numbers in parenthesis give enthalpies relative to the most stable conformers (in kcal mol^{-1}).

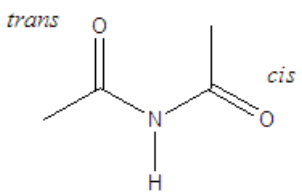

Figure 3. Definition of *cis*- and *trans*-conformations in DIAC and HFDAC.

Table 1. Total energies (*E*), enthalpies (*H*), and free energies (*G*) of the most important neutral species. Conformers denoted as in Figures 2−3. Enol and keto forms are marked with (e) and (k), respectively.

	E / hartree	*H* / hartree	*G* / hartree
ACAC-1 (e)	−345.91108	−345.77985	−345.82140
ACAC-2 (k)	−345.90254	−345.77189	−345.81514
HFAA-1 (e)	−941.52363	−941.43441	−941.48783
HFAA-2 (k)	−941.51181	−941.42337	−941.47901
HFAA-3 (k)	−941.51006	−941.42147	−941.47600
cis,trans-DIAC (k)	−361.98525	−361.86505	−361.90756
cis,cis-DIAC (k)	−361.97830	−361.85794	−361.90012
trans,trans-DIAC (k)	−361.97537	−361.85551	−361.90025
DIAC (e)	−361.97166	−361.85216	−361.89360
trans,trans-HFDAC (k)	−957.58668	−957.50877	−957.56300
cis,trans-HFDAC (k)	−957.58466	−957.50676	−957.56042
cis,cis-HFDAC (k)	−957.57375	−957.49628	−957.54830
HFDAC (e)	−957.57357	−957.49613	−957.54958

Table 2. Total energies (*E*), enthalpies (*H*), and free energies (*G*) of the most important protonated species. Conformers denoted as in Figures 4−5.

	E / hartree	*H* / hartree	*G* / hartree
H^+-ACAC-1	−346.25375	−346.10927	−346.15195
H^+-ACAC-2	−346.24938	−346.10482	−346.14690
H^+-ACAC-3	−346.24900	−346.10450	−346.14783
H^+-ACAC-4	−346.24496	−346.10046	−346.14277
H^+-HFAA-1	−941.81921	−941.71680	−941.77132
H^+-HFAA-2	−941.81659	−941.71425	−941.76735
H^+-HFAA-3	−941.81614	−941.71390	−941.76831
H^+-HFAA-4	−941.79876	−941.69652	−941.75199
H^+-DIAC-1	−362.32650	−362.19416	−362.23635
H^+-DIAC-2	−362.31603	−362.18333	−362.22563
H^+-DIAC-3	−362.28855	−362.15585	−362.19976
H^+-HFDAC-1	−957.87789	−957.78756	−957.84105
H^+-HFDAC-2	−957.87072	−957.78020	−957.83486
H^+-HFDAC-3	−957.86859	−957.77819	−957.83148
H^+-HFDAC-4	−957.84012	−957.74972	−957.80538

RESULTS AND DISCUSSION

Neutral Molecules

It is well established that ACAC adopts asymmetrical hydrogen bonded structure in its most stable conformation,[12–15] while for its hexafluoroderivative HFAA symmetrical hydrogen bonded structure with the OH···O angle close to 180 degrees has been proposed from gas-phase electron diffraction studies.[16,17] However, our earlier semiempirical calculations[29] and recent DFT study by Buemi[12] suggest that the most stable structure of HFAA should be the asymmetrical hydrogen bonded one, similar to ACAC. Our calculations indicate in accordance with earlier works that both ACAC and HFAA exist in the gas phase in hydrogen bonded enol form. In contrast, for DIAC both experimental[30] and computational[31] studies suggest that *cis, trans*-keto form is the most stable. Experimental studies both in the gas phase[32] and solid state[33] predict *trans, trans*-structure for HFDAC.

Our calculations predict that the hydrogen bonded form (ACAC-1) is in case of acetylacetone by 5.0 kcal

Table 3. Total energies (*E*), enthalpies (*H*), and free energies (*G*) of the most important Li^+ complexes. Conformers denoted as in Figure 6.

	$\frac{E}{\text{hartree}}$	$\frac{H}{\text{hartree}}$	$\frac{G}{\text{hartree}}$
Li^+–ACAC-1	−353.29232	−353.15823	−353.20294
Li^+–ACAC-2	−353.28258	−353.14723	−353.19137
Li^+–HFAA-1	−948.86778	−948.77577	−948.83404
Li^+–HFAA-2	−948.86876	−948.77561	−948.83191
Li^+–HFAA-3	−948.86521	−948.77201	−948.82786
Li^+–DIAC-1	−369.37909	−369.25487	−369.30033
Li^+–DIAC-2	−369.43922	−369.22500	−369.27058
Li^+–HFDAC-1	−964.95014	−964.86818	−964.92365
Li^+–HFDAC-2	−964.93151	−964.84955	−964.90516

Table 4. Calculated (B3LYP/6-311+G**) and experimental gas-phase proton and lithium cation affinities and basicities

	Calc.		Exp.	Calc.		Exp.[a]
	$\frac{\text{PA}(\Delta H)}{\text{kcal mol}^{-1}}$	$\frac{\text{GB}(\Delta G)}{\text{kcal mol}^{-1}}$	$\frac{\text{GB}(\Delta G)}{\text{kcal mol}^{-1}}$	$\frac{\text{LCA}(\Delta H)}{\text{kcal mol}^{-1}}$	$\frac{\text{LCB}(\Delta G)}{\text{kcal mol}^{-1}}$	$\frac{\text{LCB}(\Delta G)}{\text{kcal mol}^{-1}}$
ACAC	208.2	200.7	200.0[b]	60.13	52.63	43.1
HFAA	178.7	171.2	173.8[c]	36.90	30.46	27.3
DIAC	208.0	199.6	-	67.31	59.68	-
HFDA	176.4	167.8	172.3[c]	48.23	39.53	35.2

[a] From Ref. 11. [b] From Ref. 23. [c] From Ref. 24.

mol^{-1} more stable than energetically next stable conformation (keto form ACAC-2, with non-planar heavy-atom framework, carbonyl oxygens rotated away from each other by 180 degrees, see Figure 2) in accord with recent experimental (2.2−4.3 kcal mol^{-1})[34,35] and G2MP2 results (2.1 kcal mol^{-1} (Ref. 18) and by at least 11 kcal mol^{-1}more stable than other enol forms (without hydrogen bond).

The asymmetrical hydrogen bonded conformer (HFAA-1) is the most stable structure of HFAA. The two next stable ones are keto forms (HFAA-2 and HFAA-3), which are by 6.9 and 8.1 kcal mol^{-1} (with carbonyl oxygens rotated away from each other by *ca*. 60 and 180 degrees, respectively, see Figure 3) less stable than the most stable hydrogen bonded enol form.

DIAC exists in the gas phase in keto form according to our calculations and earlier experimental[30] and computational[31] studies. Three conformations are possible about the C−N bonds (see Figure 3). According to our calculations the most stable form is the *cis, trans*-form, which is respectively by 4.5 and 6.0 kcal mol^{-1} more stable than *cis, cis*- and *trans, trans*-forms. Those results somewhat contradict to earlier results, where it was found that after *cis, trans*-form, the *trans, trans*-form is next in stability (by 6.0 or 5.0 kcal mol^{-1} less stable than *cis, trans*-form, at HF/3-21G[36] and MP2/6-31G*//HF/4-31G*[37] levels of theory) and the *cis, cis*-form is the least stable (by 11.0 or 6.2 kcal mol^{-1} less stable than *cis, trans*-form, at HF/3-21G[36] and MP2/6-31G*//HF/4-31G*[37] levels of theory). The most stable enol form (with intramolecular hydrogen bond) is by 8.1 kcal mol^{-1} less stable than *cis, trans*-keto form.

The most stable form of HFDAC in the gas phase is *trans, trans*-keto form in accordance with experiment,[32] followed by *cis, trans*-keto form (1.3 kcal mol^{-1} less stable than *trans, trans*-keto form), *cis, cis*-keto form (7.8 kcal mol^{-1} less stable than *trans, trans*-keto form) and hydrogen bonded enol form (7.9 kcal mol^{-1} less stable than *trans, trans*-keto form).

Protonated Molecules

The most stable protonated form of ACAC is that of hydrogen bonded enol form where the proton adds to the carbonyl oxygen in the heavy atom plane so that both O−H bonds have the same direction (see structure H^+–ACAC-1 in Figure 4). Only 2.8 and 3.0 kcal mol^{-1} less stable are two forms (structures H^+–ACAC-2 and H^+–ACAC-3 in Figure 4). In the first of them (H^+–ACAC-2) the hydrogen bond is missing, *i.e.* the corresponding O−H bond is rotated 180 degrees, so that both O−H groups are *cis* to their neighboring methyl groups, and in second one (H^+–ACAC-3) is obtained by

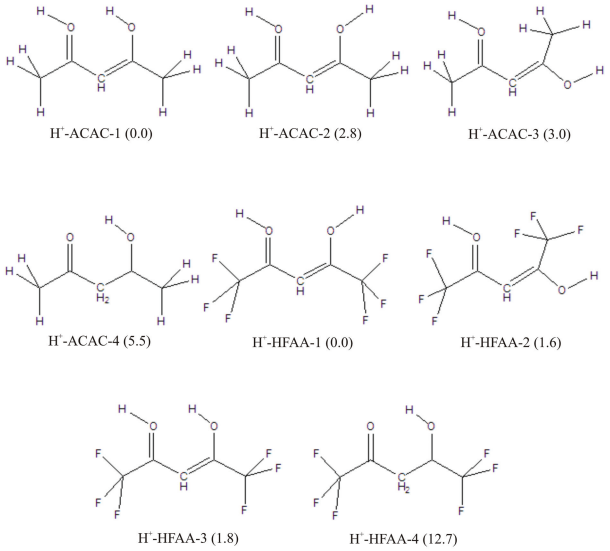

Figure 4. The most important conformations of protonated ACAC and HFAA. The numbers in parenthesis give enthalpies relative to the most stable conformers (in kcal mol^{-1}).

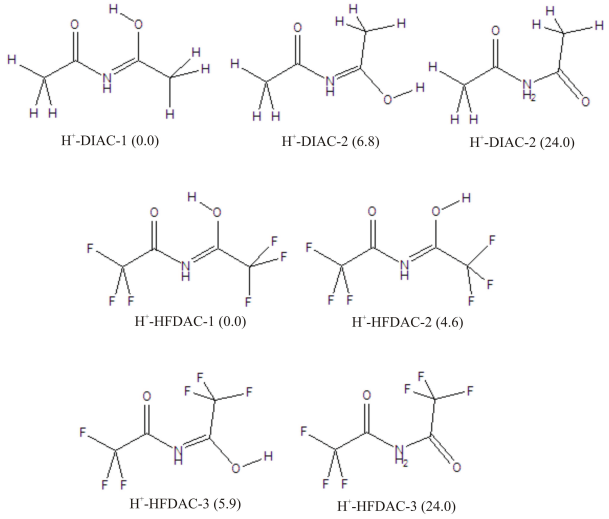

Figure 5. The most important structures of protonated DIAC and HFDAC. The numbers in parenthesis give enthalpies relative to the most stable conformers (in kcal mol^{-1}).

rotating one acetyl group (in previous form) by 180 degrees. The proposed protonated ketone form (see Figure 1, H^+–ACAC-4 in Table 2) is 5.5 kcal mol^{-1} less stable than the most stable form (H^+–ACAC-1).

In case of HFAA the most stable protonated form is the one with both carbonyl groups protonated, both *trans* relative to C−H bond, and O−H groups *cis* relative to trifluoromethyl groups (structure H^+–HFAA-1 in Figure 4). Such conformational preference is most probably caused by relatively strong interactions between O−H hydrogen and fluorines in trifluoromethyl groups as evidenced by the location of one fluorine of both CF_3 groups in the plane defined by C−C−O−H atoms and relatively short distances between fluorine and hydrogen atoms (2.058 Å).

The bonding between O−H hydrogens and fluorines in trifluoromethyl groups is further confirmed by the topological charge density analysis[38] using AIMPAC program package. There are bond critical points[38] between mentioned hydrogens and fluorines. The small values of charge densities[38] at those critical points (approximately a magnitude smaller than in O−H bonds) and positive values of the Laplacian (sum of derivatives) of charge density[38] indicate that the bonding is essentially ionic.

The second stable conformation (1.6 kcal mol^{-1} less stable, structure H^+–HFAA-2 in Figure 4) is obtained from H^+–HFAA-1 by rotation of one of acetyl groups by 180 degree and retains both (O−)H···F contacts. The next in the stability order (1.8 kcal mol^{-1} less stable than the most stable one, H^+–HFAA-1, structure H^+–HFAA-3 in Figure 4) is hydrogen bonded, O-protonated form, where only one (O−)H···F contact remains. The carbon protonated form (protonated keto-form H^+–HFAA-4) is by 12.7 kcal mol^{-1} less stable than the most stable form.

For DIAC where the neutral was in *cis, trans*-keto form, the most stable protonated form is *trans, trans*-with proton bound to one of the carbonyl oxygens and giving hydrogen bond to the other (H^+–DIAC-1, see Figure 5), *i.e.* structure analogous to that of the most stable conformer of ACAC. Other O protonated forms are at least 6.8 kcal mol^{-1} less stable (H^+–DIAC-2) and the most stable N-protonated form (H^+–DIAC-3) is by as much as 24 kcal mol^{-1} less stable than the most stable form.

The protonation of HFDAC occurs also at one of the carbonyl oxygens (see Figure 5) and the most stable form is giving hydrogen bond to the other oxygen, resulting in structure (H^+–HFDAC-1) similar to that of neutral HFAA. The *trans, trans*-structure with hydrogen bond to one fluorine of CF_3 group (H^+–HFDAC-2) is by 4.6 kcal mol^{-1} less stable and analogous *cis, trans*-structure (H^+–HFDAC-3) is by 5.9 kcal mol^{-1} less stable than the most stable one. The most stable N protonated form (H^+–HFDAC-4) is similar to DIAC by 24 kcal mol^{-1} less stable than the most stable form.

One can conclude that the protonation mechanism proposed earlier[11] is completely wrong - the neutral diacetamides exist as keto forms, so that protonation occurs at carbonyl oxygens, and in case of acetylacetones the protonation does not occur at central carbon but rather at carbonyl oxygens.

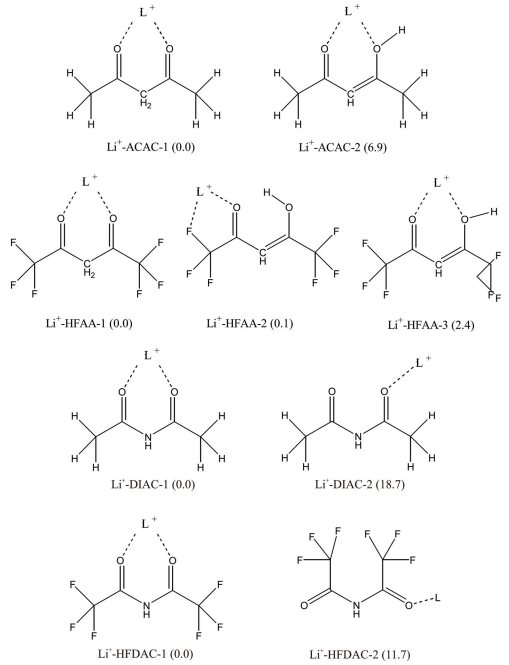

Figure 6. The most stable conformations of lithium cation adducts of ACAC, HFAA, DIAC, and HFDAC. The numbers in parenthesis give enthalpies relative to the most stable conformers (in kcal/mol).

Chelation with Lithium Cation

The lithium cation binding to the studied bases always involves both carbonyl oxygens in the most stable complexes and always corresponds to the *trans, trans*-keto form of neutral molecule (see Figure 6). The Li−O bonding with both carbonyl oxygens is symmetric as evidenced by equal bond distances. Similar structure was recently proposed for lithium complex of ACAC from solution studies.[39] In case of acetylacetone the second stable form is enol form (Li^+−ACAC-2), with lithium still bound to both oxygens, and O−H proton in *cis*-position relative to methyl group. This form is by 6.9 kcal mol^{-1} less stable. For HFAA the second most stable form is cyclic enol form with lithium cation bound to carbonylic oxygen and also to fluorine of trifluoromethyl group (structure Li^+–HFAA-2 in Figure 6, by only 0.1 kcal mol^{-1} less stable than Li^+–HFAA-1). The enol form, with lithium still bound to both oxygens, and O−H proton in *cis*-position relative to CF_3 group (structure Li^+–HFAA-3) is by 2.4 kcal mol^{-1} less stable than the most stable complex.

In case of DIAC the non-cyclic lithium cation adduct (Li^+−DIAC-2) is by 18.7 kcal mol^{-1} less stable than most stable cyclic one (Li^+−DIAC-1). The next stable conformer of lithium cation bound hexafluorodiacetamide after Li^+−HFDAC-1 is by 11.7 kcal mol^{-1} less stable (Li^+−HFDAC-2) and involve close Li^+–F contacts, indicating similar to protonated forms relatively strong interactions between them.

The lithium cation binding to the studied bases thus fully correspond to the mechanism proposed earlier,[11] contrary to protonation case. The assumption[11] that proton and Li^+ bind to different basicity centers thus does not hold, as both of them bind to carbonyl oxygens. The binding mechanisms are similar for DIAC and HFDAC, while for ACAC and HFAA the lithium cation binding involves hydrogen (or proton) displacement at carbonyl oxygen and movement of the same hydrogen to the central carbon, while protonation simply involves the addition of proton to (free) carbonyl oxygen with possible rotation of O−H bond.

CONCLUSION

The calculations indicate that both proton and lithium cation bind to carbonyl oxygens of studied bases. In case of DIAC and HFDAC both H^+ and Li^+ form cyclic adducts, based on *trans*, *trans*-keto form of base. Similar adducts are formed also between lithium cations and ACAC or HFAA, while the protonation of ACAC and HFAA occurs on carbonyl oxygens without conversion of base to the keto form.

Acknowledgements. The authors gratefully acknowledge the financial support of this research by the Estonian Science Foundation grants 5196 and 6695.

REFERENCES

1. R. L. Woodin, F. A. Houle, and W. A. Goddard, *Chem. Phys.* **14** (1976) 461−468.
2. J.-L. M. Abboud, M. Yanez, J. Elguero, D. Liotard, M. Essefar, M. El Mouhtadi, and R. W. Taft, *New J. Chem.* **16** (1992) 739−745.
3. M. Alcami, O. Mo, and M. Yanez, *J. Phys. Chem.* **93** (1989) 3929−3936.
4. M. Alcami, O. Mo, J. J. G. de Paz, and M. Yanez, *Theor. Chim. Acta* **77** (1990) 1−15.
5. P. Speers and K. E. Laidig, *J. Chem. Soc., Perkin Trans. 2* (1994) 799−806.
6. M. Alcami, O. Mo, M. Yanez, F. Anvia, and R. W. Taft, *J. Phys. Chem.* **94** (1990) 4796−4804.
7. F. Anvia, S. Walsh, M. Capon, I. A. Koppel, R. W. Taft, J. L. G. de Paz, and J. Catalan, *J. Am. Chem. Soc.* **112** (1990) 5095−5097.
8. M. Alcami, O. Mo and M. Yanez, *Modelling Intrinsic Basicities: the Use of the Electrostatic Potentials as Atoms-in-molecules Theory,* in: S. J. Murray and K. Sen (Eds.), *Molecular Electrostatic Potentials*, Elsevier, 1996, pp. 407−456.
9. R. D. Wieting, R. H. Staley, and J. L. Beauchamp, *J. Am. Chem. Soc.* **97 (**1975) 924−926.
10. R. W. Taft, F. Anvia, J.-F. Gal, S. Walsh, M. Capon, M. C. Holmes, K. Hosn, G. Oloumi, R. Vasanwala, and S. Yazdani, *Pure Appl. Chem.* **62** (1990) 17−23.
11. P. Burk, I. A. Koppel, I. Koppel, R. Kurg, J.-F. Gal, P.-C. Maria, M. Herreros, R. Notario, J.-L. M. Abboud, F. Anvia, and R. W. Taft, *J. Phys. Chem. A* **104** (2000) 2824−2833.
12. G. Buemi, *J. Mol. Struct. (Theochem)* **499** (2000) 21−34.

13. K. Iijima, A. Ohnogi, and S. Shibata, *J. Mol. Struct.* **156** (1987) 111−118.
14. A. Camerman, D. Mastropaolo, and N. Camerman, *J. Am. Chem. Soc.* **105** (1983) 1584−1586.
15. M. A. Rios and J. Rodriguez, *J. Mol. Struct. (Theochem)* **63** (1990) 137−144.
16. J. J. Dannenberg and R. Rios, *J. Phys. Chem.* **98** (1994) 6714−6718.
17. N. Nagashima, S. Kudoh, M. Takayanagi, and M. Nakata, *J. Phys. Chem. A* **105** (2001) 10832−10838.
18. A. Akrour, Z. Chikh, F. Djazi, M. Elbannaya, F. B. Berruyer, and G. Bouchoux, *Int. J. Mass Spec.* **267** (2007) 63−80.
19. A. L. Andreassen, D. Zebelman, and S. H. Bauer, *J. Am. Chem. Soc.* **93** (1971) 1148−1152.
20. K. Iijima, Y. Tanaka, and S. Onuma, *J. Mol. Struct.* **268** (1992) 315−318.
21. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
22. J. B. Foresman and A. E. Frisch, *Exploring Chemistry with Electronic Structure Methods,* 2nd Ed., Gaussian, Pittsburgh, 1997, pp. 166−168.
23. E. P. Hunter and S. G. Lias, *Proton Affinity Evaluation*, in: P. J. Linstrom and W. G. Mallard (Eds.), *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, July 2001, National Institute of Standards and Technology, Gaithersburg MD, 20899 (http://webbook.nist.gov).
24. I. A. Koppel, F. Anvia, and R. W. Taft, *J. Phys. Org. Chem.* **7** (1994) 717−728.
25. P. Burk, I. A. Koppel, I. Koppel, I. Leito, and O. Travnikova, *Chem. Phys. Lett.* **323** (2000) 482−489.
26. J. M. L. Martin and G. de Oliveira, *J. Chem. Phys.* **111** (1999) 1843−1856.
27. S. Parthiban and J. M. L. Martin, *J. Chem. Phys.* **114** (2001) 6014−6029.
28. P. Burk, M.-L. Sults, and J. Tammiku-Taul, *Proc. Estonian Acad. Sci. Chem.* **56** (2007) 107−121.
29. P. Burk and I. A. Koppel, *J. Mol. Struct. (Theochem)* **101** (1993) 277−282.
30. K. L. Gallaher and S. H. Bauer, *J. Chem. Soc., Faraday Trans. 2* **71** (1975) 1423−1435.
31. M. T. Nguyen, N. Leroux, and T. Zeegers-Huyskens, *J. Chem. Soc., Faraday Trans.* **93** (1997) 33−41.
32. N. N. Chipanina, A. M. Shulunova, T. I. Yushmanova, L. I. Volkova, and V. A. Lopyrev, *Izv. Akad. Nauk SSSR, Seriya Khim.* **12** (1988) 2852−2854.
33. P. M. Narula, C. S. Day, B. A. Powers, M. A. Odian, A. Lachgar, W. T. Pennington, and R. E. Noftle, *Polyhedron* **12** (1999) 1751−1759.
34. M. Temprado, M. V. Roux, P. Umnahanant, H. Zhao, and J. S. Chickos, *J. Phys. Chem. B* **109** (2005) 12590−12595.
35. M. M. Folkendt, B. E. Weiss-Lopez, J. P. Chauvel, and N. S. True, *J. Phys. Chem.* **89** (1985) 3347−3352.
36. G. A. Jeffrey, J. R. Ruble, R. K. McMullan, D. J. Defrees, J. S. Binkley, and J. A. Pople, *Acta Crystallogr., Sect. B* **36** (1980) 2292−2299.
37. F. Ramondo, S. N. Cesaro, and L. Bencivenni, *J. Mol. Struct.* **291** (1993) 219−244.
38. R. F. W. Bader, *Atoms in Molecules: a Quantum Theory,* Oxford Press, New York, 1990, pp. 13−40.
39. Y. Pocker and G. T. Spyridis, *J. Am. Chem. Soc.* **124** (2002) 10373−10380.

SAŽETAK

Vezanje protona i litijevog kationa na neke β-dikarbonilne spojeve

Peeter Burk, Kristo Taul i Jaana Tammiku-Taul

Institute of Chemistry, Tartu University, 2 Jakobi St., Tartu, 51014, Estonia

DFT B3LYP/6-311+G** računi sprovedeni su radi proučavanja vezanja protona i litijevog kationa na acetilaceton, heksafluoroacetilaceton, diacetamid i heksafluorodiacetamid. Pokazano je da najstabilniji kompleks Li^+ kationa uvijek odgovara cikličkoj strukturi baziranoj na *trans*, *trans*-keto formi baze. Ponađeno je da je produkt protoniranja slična ciklička *trans*, *trans*-keto forma baze u slučaje diacetamida i heksafluoroacetamida, dok u slučaju acetilacetona i heksafluoroacetilacetona protoniranje jednostavno podrazumijeva adiciju protona na (slobodnu) karbonilnu skupinu postojeće cikliziranе enolne forme baze uz moguću rotaciju O–H kemijske veze.