# MINDO/3 Investigation of the Structure of the Intramolecularly Hydrogen Bonded Enol Forms of 2-Trifluoroacetylcycloalkanones

K. A. K. Ebraheem *, S. T. Hamdi **, and A. R. Al-Derzi *

* Department of Chemistry, College of Science, and
** Department of Chemistry, College of Education, University of Basrah, Basrah, Iraq

Z. Naturforsch. **44a,** 239–242 (1989); received January 18, 1989

MINDO/3 SCF-MO calculations with full geometry optimization were performed to determine the structure of the intramolecularly hydrogen bonded enol forms of 2-trifluoroacetylcycloalkanones. The presence of two stable exocyclic and endocyclic enol forms with a non-planar unsymmetric hydrogen bonded chelate ring is established. It is found that the intramolecular hydrogen bond is weaker in the exocyclic enol of 2-trifluoroacetylcyclopentanone, which showed greater deviation from planarity by ~23.8°. The geometrical features predicted by the MINDO/3 method and the calculated charge distribution are discussed and found to agree with the available experimental data on these systems. The merits and limitations of the MINDO/3 method are discussed.

*Key words:* MINDO/3 Calculations, Fluorinated $\beta$-Diketones, Enol forms, Intramolecular H-bond.

## Introduction

Although numerous experimental investigations [1–14] and molecular orbit calculations [15–22] of varying sophistication have been reported on the structure of the intramolecularly hydrogen bonded cis enol form of acetylacetone and related molecules, they disagree on the nature of the potential energy function and the symmetry of the intramolecular hydrogen bond. Gas phase electron diffraction measurements on acetylacetone [2], trifluoroacetylacetone [3], and hexafluoroacetylacetone [4] gave short O … O non-bonded distances (2.38–2.55 Å), which has been taken as evidence for a symmetric enol form with linear hydrogen bond whereas x-ray diffraction studies on benzoylacetone [5] and dibenzoylmethane [6] suggest an asymmetric enol form with non-linear hydrogen bond. Egan and coworkers [10] have carried out $^{13}C$ and $^{2}H$ spin-relaxation time and deuterium quadrupole coupling constant measurements and concluded that the intramolecular hydrogen bond in acetylacetone is asymmetrical and that the potential energy function is of double minimum type. A similar conclusion has been drawn by Robinson and coworkers [11, 12] on the basis of UV, IR, and NMR spectra and by Tayyari et al. [13] based on IR and Raman spectroscopic studies.

The observation of two O(1) ionisation bands differing by ca. 1.5 eV in the x-ray photoelectron spectra of $\beta$-diketones [14] provided further evidence for the asymmetry of the hydrogen bridge in the enol form of $\beta$-diketones.

We have demonstrated recently [23, 24] that 2-trifluoroacetylcycloalkanones exist in solution as an equilibrium mixture of the tautomeric exocyclic and endocyclic enol forms (see Fig. 1) which interconvert very rapidly by intramolecular chelate proton transfer [24]. The two possible enol forms are distinguishable

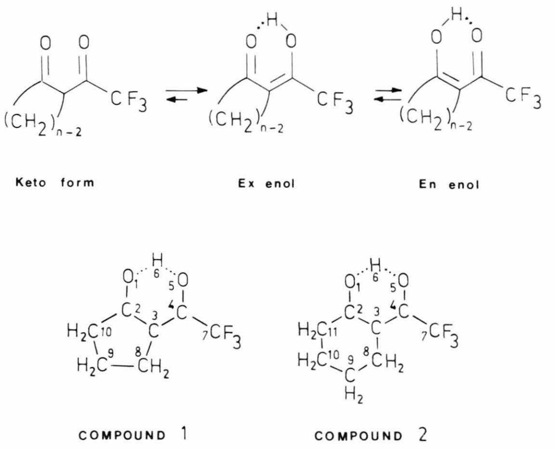

Fig. 1. The tautomeric forms of 2-trifluoroacetylcycloalkanones and the numbering system used to identify the bond lengths and angles.

---

Reprint requests to Dr. K. A. K. Ebraheem, College of Science, University of Basrah, Basrah/Iraq.

0932-0784 / 89 / 0300-0239 $ 01.30/0. – Please order a reprint rather than making your own copy.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition “no derivative works”). This is to allow reuse in the area of future scientific usage.

as individuals in the electronic and vibrational spectra [23], whereas the NMR spectra [24] correspond to a weighted average of the two species as a consequence of the rapid interconversion in comparison with the NMR time scale.

Considering the aforementioned structural problems associated with the tautomeric forms of 2-trifluoroacetylcycloalkanones, we have undertaken a MINDO/3 [25, 26] study in order to provide an understanding of the electronic and molecular structures of the enol forms in these systems.

Although, no theoretical method can be relied on a priori, the performance of the MINDO/3 method can be assessed from the very extensive tests that have been published [25–28]. Apart from documented deficiencies [29, 30], the MINDO/3 method provides satisfactory heats of formation and dipole moments [25–27]. Dewar [26, 27] has stated that the MINDO/3 values of the dipole moments are about as good as those obtained by minimum basis set ab-initio SCF calculations.

Early reports [31, 32] of the inadequacy of the MINDO/3 method to deal with hydrogen bonded systems were mainly concerned with strong intermolecular interactions between polar molecules. Such interactions are also known to be inadequately described by other semi-empirical methods such as MNDO [33] and SINDO/1 [34]. The applicability of the MINDO/3 method for the less polar interactions has recently been demonstrated for intermolecular hydrogen bonding between pairs of amino acids [35] and for intramolecular hydrogen bonding in relation to intramolecular proton transfer in diotropic reactions [36].

## Calculations

All calculations were carried out on a NEC ACOS-6 Computer of the University of Basrah Computer Centre using a modified version of the MINDO/3 program [25, 26] with standard parameters.

## Results and Discussion

MINDO/3 calculations have been performed on the intramolecularly hydrogen bonded enol forms of 2-trifluoroacetalcyclopentanone (compound **1**) and 2-trifluoroacetylcyclohexanone (compound **2**), whose structures are depicted in Figure 1. For each molecule, three series of calculations, corresponding to three initial enol structures, were carried out. In the first, related to the exocyclic enol (Ex enol), the internally bound hydrogen H 6 was initially assumed to be bonded to the trifluoroacetyl oxygen O5, whereas the second was related to the endocyclic enol (En enol), where H 6 was initially bonded to the ring carbonyl oxygen O1. Finally, the third series of calculation was performed for a symmetrical enol form. These initial geometries were then subjected to a full geometry optimization for all (3 N-6) independent bond lengths, angles and dihedral angles with no geometrical constraints.

### *Geometries and Enthalpies of Formation*

Geometry optimization was carried out by the Davidson-Fletcher-Powell method for the three initial enol structures. The final optimized geometries and enthalpies of formation are listed in Table 1. The present MINDO/3 calculations clearly establish the presence of two stable enol forms for compounds **1** and **2**. In **1**, the exocyclic enol is predicted to be more stable than the endocyclic enol, whereas for **2**, the two forms show comparable stabilities. It is of interest to note that the third series of calculation gave no indication of a stable symmetric enol structure for either molecule, and in each case the calculations converged to one of the two stable enols.

The MINDO/3 results for the energy of interconversion between the endocyclic and exocyclic enol forms (0.59 kcal/mol for **1** and 0.16 kcal/mol for **2**) compare very well with the experimental values of 0.52–0.2 kcal/mol reported by Koltsou [37] for other $\beta$-diketones and are in keeping with the observed rapid interconversion between the two forms [24].

The final optimized geometries listed in Table 1 for compounds **1** and **2** clearly show that MINDO/3 predicts a non-planar unsymmetric six-membered intramolecularly hydrogen bonded chelate ring with a non-linear OHO bridge (the O1–H6–O5 angle is ~118°; see Table 1). The exocyclic enol form of compound **1** shows the highest deviation from planarity (by ~23.8°). This is probably due to a higher ring strain in the five-membered ring system. In contrast to acetylacetone and other acyclic $\beta$-diketones, where the chelate ring is considered to be planar [16], it does not necessarily follow that the planar structure is the most stable in strained cyclic $\beta$-diketones with bulky

Table 1. MINDO/3 optimized geometries and enthalpies of formation of 2-trifluoroacetylcyclopentanone (**1**) and 2-trifluoroacetylcyclohexanone (**2**).

| Geometric Parameters [a] | Compound **1** | | Compound **2** | |
|---|---|---|---|---|
| | En form | Ex form | En form | Ex form |
| Bond lengths | | | | |
| C2–O1 | 1.303 | 1.204 | 1.307 | 1.210 |
| C3–C2 | 1.388 | 1.506 | 1.390 | 1.507 |
| C4–C3 | 1.483 | 1.378 | 1.490 | 1.387 |
| O5–C4 | 1.204 | 1.309 | 1.206 | 1.306 |
| C7–C4 | 1.505 | 1.489 | 1.502 | 1.490 |
| H6–O1 | 0.951 | 2.831 | 0.951 | 2.478 |
| H6–O5 | 2.887 | 0.952 | 2.533 | 0.951 |
| C8–C3 | 1.530 | 1.528 | 1.526 | 1.523 |
| C10–C2 (1) | 1.518 | 1.527 | – | – |
| C11–C2 (2) | – | – | 1.521 | 1.527 |
| C–C (ring) | 1.526 | 1.526 | 1.520 | 1.520 |
| C–H (ring) | 1.120 | 1.120 | 1.120 | 1.120 |
| C7–F (aver.) | 1.350 | 1.350 | 1.350 | 1.350 |
| O1 ... O5 | 3.446 | 3.394 | 3.142 | 3.065 |
| Bond angles | | | | |
| C3–C2–O1 | 132.15 | 126.56 | 127.89 | 121.84 |
| C4–C3–C2 | 132.93 | 133.55 | 127.82 | 126.71 |
| O5–C4–C3 | 127.93 | 131.91 | 127.43 | 132.74 |
| H6–O1–C2 | 116.38 | – | 118.20 | – |
| H6–O5–C4 | – | 116.56 | – | 118.27 |
| C7–C4–C3 | 108.97 | 116.59 | 111.94 | 118.31 |
| C8–C3–C2 | 107.86 | 108.30 | 115.63 | 117.00 |
| C10–C2–C3 (1) | 113.38 | 106.95 | – | – |
| C11–C2–C3 (2) | – | – | 124.97 | 118.60 |
| C9–C10–C2 (1) | 107.01 | 107.30 | – | – |
| C10–C11–C2 (2) | – | – | 117.28 | 120.65 |
| C9–C8–C3 | 106.68 | 106.30 | 116.78 | 116.72 |
| C10–C9–C8 | 107.31 | 107.86 | 113.11 | 114.86 |
| C11–C10–C9 | – | – | 115.42 | 117.44 |
| C4–C7–F (aver.) | 105.34 | 106.26 | 104.03 | 106.01 |
| O1 ... H6 ... O5 | 118.70 | 118.82 | 121.98 | 119.90 |
| Dihedral angles [b] | | | | |
| C4–C3–C2–O1 | 7.35 | 23.87 | 5.54 | 7.83 |
| O5–C4–C3–C2 | −34.36 | −13.16 | 17.78 | −5.45 |
| H6–O5–C4–C3 | – | −5.73 | – | −2.10 |
| H6–O1–C2–C3 | 1.66 | – | −0.52 | – |
| C7–C4–C3–C2 | 147.12 | 166.41 | 192.43 | 174.64 |
| C8–C3–C2–O1 | 180.91 | 194.90 | 186.98 | 187.23 |
| C9–C8–C3–C2 | −7.13 | −16.30 | 328.58 | 325.43 |
| C10–C9–C8–C3 | 8.08 | 11.67 | 48.27 | 45.79 |
| C11–C10–C9–C8 | – | – | 319.93 | 330.09 |
| $\Delta H_f$ (kcal/mol) | −283.61 | −284.20 | −290.45 | −290.61 |

[a] Bond lengths in Å; angles in degrees; see Fig. 1 for numbering system.
[b] Dihedral angle A–B–C–D is defined as the clockwise rotation of C–D from A–B, as seen in the direction B → C.

$CF_3$ substituents. Destabilizing non-bonded interactions between the proximal H atoms of the ring methylene groups ($CH_2$), together with the steric influence of the bulky $CF_3$ group, could lead to a non-planar chelate ring being the most stable.

Table 2. Calculated dipole moments (in Debye) and net charge densities of the enol forms of compounds **1** and **2**.

| Property [a] | Compound **1** | | Compound **2** | |
|---|---|---|---|---|
| | En form | Ex form | En form | Ex form |
| Dipole moments | 4.734 | 3.295 | 4.851 | 3.904 |
| Charge densities | | | | |
| O1 | −0.4239 | −0.5092 | −0.4367 | −0.5299 |
| C2 | 0.4734 | 0.5965 | 0.4873 | 0.5939 |
| C3 | −0.3636 | −0.3174 | −0.3609 | −0.3166 |
| C4 | 0.5113 | 0.3291 | 0.5209 | 0.3452 |
| O5 | −0.4737 | −0.4100 | −0.4957 | −0.4124 |
| H6 | 0.2784 | 0.2794 | 0.2821 | 0.2851 |
| C7 | 0.9936 | 1.0317 | 0.9941 | 1.0147 |
| C8 | 0.1330 | 0.1238 | 0.1383 | 0.1374 |
| C10 | 0.0014 | −0.0680 | – | – |
| C11 | – | – | −0.0014 | −0.0645 |
| F (aver.) | −0.4036 | −0.3876 | −0.4059 | −0.3858 |

[a] See Fig. 1 for numbering system.

In going from the endocyclic enol (En enol) to the exocyclic enol (Ex enol) the following interesting features are noteworthy. Firstly, the non-bonded O1 ... O5 distance decreases, resulting in a decrease in the intramolecular hydrogen bond (H6 ... O) distance. Secondly, the C–C bond of the chelate ring (i.e. C4–C3 in En and C3–C2 in Ex) increases, while the C=C bond (i.e. C3–C2 in En and C4–C3 in Ex) decreases. This is in accord with the loss of π-electron delocalisation in the exocyclic enol form as evidenced by the greater deviation from planarity in comparison with the endocyclic enol form (see Table 1).

The ring size effects on the strength of intramolecular hydrogen bond is also evident in the present MINDO/3 calculations. The non-bonded O1 ... O5 and H6 ... O distances are longer in compound **1** indicating a relatively weaker hydrogen bond in the strained five-membered ring system.

The aforementioned geometrical features predicted by the MINDO/3 method correlate with several properties of the enols of compounds **1** and **2**. The weaker hydrogen bond in **1** in comparison with **2** is consistent with the observed [24] higher acidity in **1** (compare $pK_a$ values: compound **1**, 6.75; compound **2**, 7.18) and the observed [24] higher shielding of the enolic OH proton NMR signal ($\delta$(OH): compound **1**, 13.011 ppm; compound **2**, 15.061 ppm). The loss of π-electron delocalization in the exocyclic enol form of **1** is in keeping with the observed electronic spectral data [23], where the $\pi \rightarrow \pi^*$ transition is observed at 277 and 303 nm for **1** and **2**, respectively.

The present MINDO/3 calculations gave a value of 1.35 Å for the C–F bond length, in satisfactory agreement with the observed value of 1.34 Å reported [3, 4] for other fluorinated acyclic $\beta$-diketones, but overestimate the C–H bond lengths, which is known to be a systematic error of the MINDO/3 method [30].

### *Charge Distribution*

The calculated net charge densities and dipole moments for the two possible enol forms of compounds **1** and **2** are shown in Table 2. It is hoped that the relative changes in charge distribution can be correlated with changes in geometry of the two interconverting enols and hence provide further insight into changes in bonding involved.

The MINDO/3 results (Table 2) clearly show that the H atom in the hydrogen bridge is positively charged, while the oxygen atoms of both the O–H donor group and the C=O acceptor group are negatively charged, in agreement with the results on other hydrogen bonded systems [38]. However, the magnitude of these charges decreases as the O1 ... O5 distance increases. Another interesting feature is the accumulation of large positive charge on the C7 atom of the $CF_3$ group, which also seems to correlate inversely with the O1 ... O5 distance. These changes also correspond to an increase in the molecular dipole moment, which shows strong dependence on the structure of the enol. Thus, it seems reasonable to suggest that the two enol forms may differ in their susceptibilities for polar interactions with the solvent due to differences in their dipole moments and charge distribution.

[1] K. I. Pashkevich, V. I. Saloutin, and I. Ya. Postovskii, Russ. Chem. Rev. **50,** 180 (1981); and references cited therein.
[2] A. H. Lowrey, C. George, P. D. Antonio, and J. Karle, J. Amer. Chem. Soc. **93,** 6399 (1971).
[3] A. L. Andreassen and S. H. Bauer, J. Mol. Struct. **12,** 381 (1972).
[4] A. L. Andreassen, D. Zebelman, and S. H. Bauer, J. Amer. Chem. Soc. **93,** 1148 (1971).
[5] D. Semmingsen, Acta Chem. Scand. **26,** 143 (1972).
[6] D. E. Williams, Acta Crystallogr. **21,** 340 (1966).
[7] N. N. Shapet'ko, Org. Magn. Reson. **5,** 215 (1973).
[8] H. Ogoshi and K. Nakamoto, J. Chem. Phys. **45,** 3113 (1966).
[9] H. Musso and H. Junge, Chem. Ber. **101,** 801 (1968).
[10] W. Egan, G. Gunnarsson, T. E. Bull, and S. Forsen, J. Amer. Chem. Soc. **99,** 4568 (1977).
[11] M. J. T. Robinson, K. M. Rosen, and J. D. B. Workman, Tetrahedron **33,** 1655 (1977).
[12] J. C. J. Barna and M. J. T. Robinson, Tetrahedron (Lett.) **1979,** 1455.
[13] S. F. Tayyari, T. Zeegers-Huyskens, and J. L. Wood, Spectrochim. Acta **35 A,** 1289 (1979).
[14] R. S. Brown, J. Amer. Chem. Soc. **99,** 5497 (1977).
[15] P. Schuster, Chem. Phys. (Lett.) **3,** 433 (1969).
[16] M. S. Gordon and R. D. Koob, J. Amer. Chem. Soc. **95,** 5863 (1973).
[17] A. D. Issacson and K. Morokuma, J. Amer. Chem. Soc. **97,** 4453 (1975).
[18] G. Karlstrom, H. Wennerstrom, B. Jonsson, S. Forsen, J. Almloff, and B. Roos, J. Amer. Chem. Soc. **97,** 4188 (1975).
[19] D. L. Breen, J. Phys. Chem. **82,** 714 (1978).
[20] J. E. Del Bene and W. L. Kochenour, J. Amer. Chem. Soc. **98,** 2041 (1976).
[21] P. George, C. W. Böck, and M. Trachtman, J. Mol. Struct. (Theochem) **92,** 109 (1983).
[22] S. Millefiori, A. Millifiori, and G. Granozzi, J. Mol. Struct. (Theochem) **105,** 135 (1983).
[23] K. A. K. Ebraheem, S. T. Hamdi, and M. N. Khalaf, Can. J. Spectrosc. **26,** 225 (1981).
[24] K. A. K. Ebraheem and S. T. Hamdi, submitted for publication.
[25] R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Amer. Chem. Soc. **97,** 1285 (1975).
[26] R. C. Bingham, M. J. S. Dewar, and D. H. Lo, J. Amer. Chem. Soc. **97,** 1294 (1975); **97,** 1302 (1975); **97,** 1307 (1975).
[27] M. J. S. Dewar, Chem. Ber. **11,** 97 (1975).
[28] M. J. S. Dewar, J. Phys. Chem. **89,** 2145 (1985).
[29] M. J. S. Dewar and W. Thiel, J. Amer. Chem. Soc. **99,** 4907 (1977).
[30] S. P. McManus and M. R. Smith, Tetrahedron (Lett.) **1978,** 1897.
[31] T. J. Zielinski, D. L. Breen, and R. Rien, J. Amer. Chem. Soc. **100,** 6266 (1978).
[32] G. Klopman, P. Andreozzi, A. J. Hopfinger, O. Kikuchi, and M. J. S. Dewar, J. Amer. Chem. Soc. **100,** 6267 (1978).
[33] M. J. S. Dewar and G. P. Ford, J. Amer. Chem. Soc. **101,** 5558 (1979).
[34] K. Jug and D. N. Nanda, Theor. Chim. Acta **57,** 107 (1980).
[35] D. H. Abed and M. A. Shanshal, Iraqi J. Sci. **28,** 391 (1987).
[36] B. Ya. Simkin, B. V. Golyanskii, and V. I. Minkin, Zh. Org. Khim. **17,** 3 (1981); Chem. Abstr. **95,** 23982 x (1981).
[37] A. I. K. Kol'tsou, Zh. Org. Khim. **12,** 2036 (1976); Chem. Abstr. **86,** 71121 b (1977).
[38] P. George, C. W. Bock, and M. Trachtman, J. Mol. Struct. (Theochem) **133,** 11 (1985).