

Resonance assisted intramolecular hydrogen bonding of 6-hydroxy-6-(2-thienyl)-2-thenoylfulvene

A-R. Nekoei ^{*a}, M. Vakili ^b, S. F. Tayyari ^b, S. Salemi ^c,

^a Department of Chemistry, Shiraz University of Technology, Shiraz, 71555-313, Iran

^b Department of Chemistry, Ferdowsi University of Mashhad, Mashhad 91774-1436, Iran

^c Department of Chemistry, Sabzevar Tarbiat Moallem University, Iran

Keywords: Diacylcyclopentadiene, Dithenoylcyclopentadien, Intramolecular hydrogen bond, Resonance assisted hydrogen bond.

Introduction

1,2-diacylcyclopentadiene (1,2-DACP) compounds (also known as fulvene compounds) belong to a category of γ -dicarbonyl compounds with the capability of forming intramolecular hydrogen bond (IHB) (see Fig.1). In the enol form of these compounds, as a result of IHB, and because of a long π -electronic conjugation between carbonyl and cyclopentadiene double bands, a 7-membered ring-like structure (see Fig.1) is formed which is referred to as chelated or enolone ring (like 6-membered chelated ring in β -dicarbonyls). Since the chelated ring is heptagonal [1], the spatial orientations (distances and angles) for O and H–O segments of molecule are more proper to form much stronger O \cdots H–O hydrogen bond in 1,2-DACPs, in comparison to that of β -dicarbonyls. Also the longer resonance structure of delocalized π -electrons makes the resonance assisted intramolecular hydrogen band, RAHB [2], in this type of γ -dicarbonyls to be stronger than that of β -dicarbonyls.

In the present work, 1,2-dithenoylcyclopentadien (DTCP) has been investigated with special attention to its IHB, in order to obtain detailed information on the conformational relative stabilities, structures and electron conjugation in its resonance assisted hydrogen bond (RAHB). It is also important to estimate the barrier height for proton transfer and the strength of the IHB, which is the main factor governing the conformational stability.

Method of Analysis

All quantum calculations were carried out with the GAUSSIAN 03 software package, applying the modern density functional theory, DFT, at B3LYP level using variety of basis sets.

Results and Discussion

There are 74 different keto and enol conformers for DTCP. Among 16 more stable cis-enol forms, there are only 4 chelated enol forms, i.e. the CE1, CE2, CE3, and CE4 conformers in Fig. 2, which have the seven-membered chelated ring of the IHB. These are so stable that the presence of other conformers in significant amounts in the sample is unlikely. This is predicted from all levels of calculation that the conformations CE4 and CE1 are the most stable and the most unstable chelated forms, respectively.

The barrier heights for proton transfers in the mentioned four chelated conformers of DTCP are given in Table 1. The barrier height energies, E_{BH} , for these conformers, calculated at B3LYP/6-31G** level using HC forms in Fig. 2 as transition state, are in the range of 0.31-0.39 kcal/mol. For α -cyanoacetylacetone (CNAA) and dibenzoylmethane (DBM) molecules with the strongest IHBs that have been reported for β -dicarbonyls, the proton transfer barrier heights were calculated to be 1.33 and 1.61 kcal/mol, respectively. Thus, the barriers for proton transfer in all DTCP conformers are significantly much lower than those in all mentioned β -dicarbonyls. These results also confirm that the IHB in DTCP conformers is stronger even than those in the strongest IHBs reported in β -dicarbonyls. This is confirmed by theoretical IHB energies (E_{HB}) reported in Table 1.

Comparing C=C, C-C and S-C bond lengths of each thienyl group in DTCP with the corresponding bonds of heterocyclic aromatic thiophene molecule with C_{2v} symmetry, suggest a well-oriented π -electron conjugations between the thienyl rings and the enol ring of DTCP.

It has been shown in the enol forms of β -dicarbonyl compounds that the Gilli's symmetry coordinates, q_1 ($d_{C-C} - d_{C=C}$), q_2 ($d_{C-O} - d_{C=O}$), and Q ($q_1 + q_2$) [3], offer a criterion for the bond equalization in their chelated ring due to their resonance assisted hydrogen bonding (RAHB). The values of $q_1=0.15$ and $q_2=0.17$ for the standard bond distances in the absence of π delocalization [3] lead to $Q=0.32$ for the completely π -localized enol forms, while $Q=0.0$ corresponds to the fully π -delocalized structures [2, 3]. For comparison, the calculated values for Q parameters of DTCP and several compounds with RAHD are also given in Table 1. The trend of these values is as: DTCP < DBM < BA (benzoylacetone) < TTFA (thenoyltrifluoroacetone) < CNAA < TMHD (2,2,6,6-tetramethyl-3,5-heptanedione) < AA,

from which three points can be clearly indicated. First, the resonance conjugation of phenyl, thienyl, cyclopentadiene and cyano groups assist the delocalization of π -electrons in chelated ring of IHB. Secondly, the IHB strengths (according to NMR proton chemical shift studies), which don't follow the mentioned trend of Q values, should depend on some other parameters besides the resonance assisting of functional groups in IHB. Third, the delocalization in 7-membered chelated ring of DTCP γ -dicarbonyl compound is very much more assisted compared to that in 6-membered chelated ring of β -dicarbonyl molecules.

Conclusion

The IHB in DTCP conformers is stronger even than those in the strongest IHBs reported in β -dicarbonyls. Well-oriented π -electron conjugations between the thienyl rings and the enol ring of DTCP are confirmed. Also, the delocalization in 7-membered chelated ring of DTCP γ -dicarbonyl compound has been shown to be very much more assisted compared to that in 6-membered chelated ring of β -dicarbonyl molecules.

Table 1: Gilli's symmetry parameter (Q), IHB energy (E_{HB}) and barrier height energy (E_{BH}) of DTCP and some selected β -dicarbonyls (energies in kcal/mol).

	DTCP	DBM	BA	TTFA	CNA	TMHD	AA
E_{BH}^a	0.39	1.61	NC	1.89	1.33	1.28	1.71
E_{HB}^b	19.34	16.15	16.07	13.89	16.26	17.09	15.87
Q^b	0.082	0.133	0.140	0.142	0.144	0.147	0.150

a: calculated at B3LYP/6-31G**; NC: not calculated.
b: calculated at B3LYP/6-311++G**.

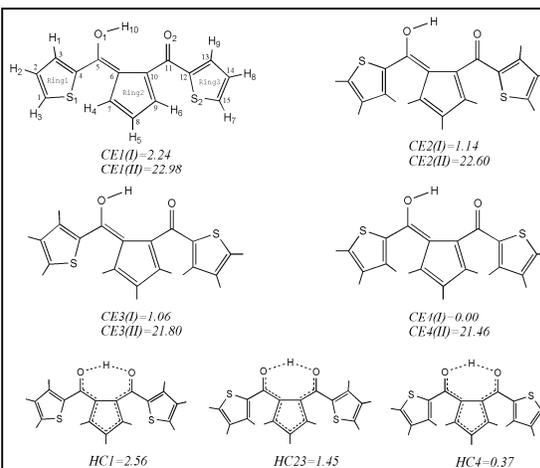
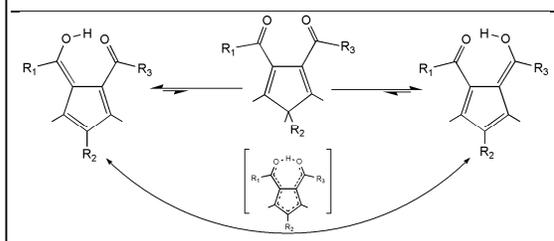


Fig 2: Cis-enol and H-centered forms of DTCP, and their relative stability, calculated at B3LYP/6-31G** level.

References

- [1] R.S. Brown, A. Tse, T. Nakashima, R.C. Haddon, *J. Am. Chem. Soc.* 101 (1979) 3157.
- [2] V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, *G. J. Chem. Soc. Perkin Trans. 2* (1997) 945.
- V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, *J. Am. Chem. Soc.* 113 (1991) 4617.