Conformational Analysis of Dimethylaminomethylene-Malonic Acid Dimethyl Ester

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The aim of this work is the conformational study and interpretation of vibrational spectra of the title compound [$(H_3C)_2N\text{-}CH{=}C(COOCH_3)_2$, DMAMDME]. This compound belongs to the family of so-called push-pull ethylenes containing electron-donor groups at one end and electron-acceptor groups at the other end. Despite the large interest in organic synthesis [1] the theoretical and experimental study of their conformers with the interpretation of vibrational spectra has not yet been carried out for many of them.

DMAMDME can exist in four *ZZ*, *EZ*, *ZE* and *EE* conformations with regard to the orientation of both methylester groups where the first and second letters express the orientation of the carbonyl oxygen to the C=C bond for *trans* and *cis* methylester group, respectively. Previous study of DMAMDME revealed that this compound exists in solid phase in *ZE* conformation with the carbonyl of *cis* methylester twisted by 68° to the plane formed by the other double bonds [2] and in nonpolar solvents no next conformers were reported [2, 3]. This work contains theoretical calculations and vibrational and NMR study as well. Theoretical calculations were carried out at the *ab initio* MP2 and DFT B3LYP level in 6-31G** basis set. According to the theoretical calculations, the *ZZ* conformer is most stable followed by *EZ* and *ZE* conformers (Table 1). Vibrational spectra in polar solvents indicate the presence of the next conformer. These experimental results are explained by the influence of environment polarity on the conformational equilibrium and are discussed with respect to the SCRF solvent effect calculations using PCM model.

Table 1: Calculated MP2 and DFT relative energies ΔE and dipole moments μ of DMAMDME conformers and their relative energies in solvents ($CHCl_3$, CH_3CN) using PCM model.

DMAM DME	ΔE(MP2) (kJ/mol)	ΔE(DFT) (kJ/mol)	μ(MP2) (D)	ΔE(MP2) (kJ/mol) ($CHCl_3$)	ΔE(MP2) (kJ/mol) (CH_3CN)	ΔE(DFT) (kJ/mol) ($CHCl_3$)	ΔE(DFT) (kJ/mol) (CH_3CN)
ZZ	0.00	0.00	2.56	0.00	0.00	0.00	0.00
EZ	4.49	5.53	4.22	4.23	3.15	4.25	3.36
ZE	5.11	7.12	4.22	2.72	1.52	3.14	1.83
EE	11.32	15.40	5.69	6.47	3.58	7.78	4.64

[1] S.F. Dyke, *The Chemistry of Enamines*; Cambridge University Press: London 1973
[2] U. Shmureli, H. Shanan-Atidi, H. Horwitz, Y. Shvo, J. Chem. Soc., Perkin Trans. II (1973) 657
[3] D. Smith, P.J. Taylor, J. Chem. Soc., Perkin Trans. II (1979) 1376

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