

Isomerizational and Conformational Study of 3-Cyclopropylamino-2-Acetyl Propenenitrile (CpAAP) and 3-Cyclopropylamino-2-Methylsulfonyl Propenenitrile (CpASP)

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(H₅C₃)-NH-CH=C(CN)(COCH₃) (CpAAP) and (H₅C₃)-NH-CH=C(CN)(SO₂CH₃) (CpASP) belong to the push-pull ethylenes intensively used in synthetic organic chemistry. The electron donor cyclopropylamino group in the investigated compounds seems to have a special influence on their conformational and configurational equilibria perhaps due to the possibility to create an intramolecular hydrogen bond.

Using ab initio MP2 and DFT B3LYP calculations in 6-31G** basis set seven conformers of CpAAP have been found, three for *Z*-isomer and four for *E*-isomer (the first letter denotes *cis* and *trans* position of cyclopropylamino and acetyl groups, the second *Z* or *E* and the third *s* or *a* letters denote the conformational orientation of carbonyl oxygen and cyclopropylamino group towards or from double C=C bond, respectively). However, as shown by calculations, they significantly differ in energy. The most stable conformer is the *ZZa* one that enables an intramolecular hydrogen bond. This conformer has been synthesized and confirmed by NMR in chloroform. *ZZa* cannot pass to other *Z*-isomer conformers. Nevertheless, in more polar DMSO only the process of isomerization takes place and the next two conformers of *E*-isomer with *anti* and *syn* orientation of cyclopropylamino group have been confirmed.

In the case of CpASP, there are only four possibilities from the conformational point of view because sulfonyl group can exist only in a single orientation towards the double C=C bond (one S=O bond coplanar with C=C bond, the second S=O bond and methyl group above and below this plane). Therefore we can consider for both *E* and *Z* isomers only the *anti* (*a*) or *syn* (*s*) conformational positions of cyclopropylamino group (second letter). Because the cyclopropylamino group is also oriented out of the plane of olefinic skeleton, its position toward the methyl group is given by the third letter *a* or *s* (on the opposite or the same side of this plane). Analogously to CpAAP we have found by ab initio MP2 calculations that the most stable conformer is the *Zaa* one. However, in the synthetic process the pure *E*-isomer has been obtained. In DMSO the presence of both *E*-isomer conformers has been proven both by NMR and vibrational spectroscopy with *Eaa* conformer as the more stable one. Additionally, in less polar chloroform an isomerization process occurred and the *Z*-isomer has been detected as well. In order to explain such behavior, solvent effect calculations using PCM model have been done.

Table 1: MP2/6-31G** calculated ab initio relative energies ΔE of CpAAP and CpASP conformers.

CpAAP	<i>EZa</i>	<i>EZs</i>	<i>EEa</i>	<i>EEs</i>	<i>ZZa</i>	<i>ZZs</i>	<i>ZEa</i>
ΔE(kJ/mol)	14.93	19.68	28.09	37.65	0.00	40.77	49.86
CpASP	<i>Eaa</i>	<i>Eas</i>	<i>Esa</i>	<i>Ess</i>	<i>Zaa</i>	<i>Zas</i>	<i>Zsa</i>
ΔE(kJ/mol)	4.28	4.58	6.17	7.08	0.00	0.60	28.73

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