化学学报 1997 55 (3): 290-295 ISSN: 0567-7351 CN: 31-1320/06

取代杂氮硅三环的核磁共振及分子动力学研究

张晓东,毛诗珍,沈联芳,吕正荣,卓仁禧

中国科学院武汉物理研究所;中国科学院波谱与原子分子物理国家重点实验;武汉大学化学系

收稿日期 修回日期 网络版发布日期 接受日期

摘要 对取代的杂氮硅三环类化合物(Silatrane)-(3R,4S)-1-氯甲基杂氮硅三环-4-羧酸(1)和(3R,4S)-1-氯甲基-3-甲基杂氮硅三环-4-羧酸(2)及它们相应的三乙基铵盐(3)和(4)的结构采用^1H,^1^3C,^2^9Si NMR进行研究, 其一维^1H NMR谱根据二维同核和异核相关谱进行了归属。从测得的偶合常数及化学位移分析, 得出羧基及其铵盐的取代造成相邻另外两环上的-CH2-CH2-O-链上二面角发生扭拐, 成为拐折旁式构象。分子动力学方法的模拟计算证明了这种构象变化。另外根据溶液中^2^9Si及^1H的化学位移实验结果, 讨论了该类化合物环上取代对分子内配键(N-Si)的影响。

关键词 碳13核磁共振谱法 氮杂环化合物 质子磁共振谱法 硅杂环化合物 构象 分子动力学 硅二十九核磁共振谱法

分类号 0657

NMR and molecular dynamics study on some substituted silatranes

ZHANG XIAODONG,MAO SHIZHEN,SHEN LIANFANG,LU ZHENGRONG,ZHUO RENXI

Abstract ^1H, ^1^3C and ^2^9Si NMR spectroscopy and molecular dynamics (MD) methods were employed to study the structure of the four synthesized silatrane compounds-(3R,4S)-1-chloromethyl silatrane-4-carboxylic acid (1), (3R,4S)-1-chloromethyl-3-methyl-silatrane-4-carboxylic acid (2), and their corresponding triethylamine salts (3), (4). The 2D ^1H-^1H COSY and ^1^3C-^1H COSY experiments and 1D spectrum simulation were carried out for assigning ^1H NMR spectrum. From the NMR data, it was derived that the substitution of 4-carboxylic acid group on the title compounds causes the atrane framework distorted, and the unsubstituted two adjacent -CH2-CH2-O- chains distorted as two staggered gauche conformations. The MD calculation supports the conclusion. Furthermore, no conformation transitions were found for the title compounds. The ^2^9Si NMR data indicate that the N-Si dative bond is weakened slightly when the substitutions of the carboxyl group and corresponding salt group in the atrane framework happen, and the effect is stronger than that of the methyl substitution on the equatorial position of the atrane framework.

Key words C13 NMR SPECTROMETRY NITROGEN HETEROCYCLICS PROTON MAGNETIC RESONANCE SPECTROMETRY SILICON HETEROCYCLICS COMPOUNDS CONFORMATION MOLECULAR DYNAMICS

DOI:

通讯作者