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论文

偶氮基杯芳烃化合物的合成及其偶氮-醌踪互变异构性质

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摘要:

通过芳胺的重氮化-偶合反应合成了8个偶氮基杯芳烃化合物, 其结构经IR, ¹H NMR, ESI-MS和元素分析表征. 通过UV-Vis, ¹H NMR和IR考察了溶液pH值对所合成化合物5,11,17,23-四[(2-苯并噻唑基)偶氮基]-25,26,27,28-四羟基杯芳烃(3)和5,17-二[(1-萘基)偶氮基]-25,26,27,28-四羟基杯芳烃(4)的偶氮-醌踪互变异构的影响. 结果表明, 随着溶液pH值增加, 醌踪体在偶氮-醌踪互变异构平衡中的比例增加, 当pH≥10时, 几乎全部转变为醌踪体. 特别当溶液pH=-1时, 化合物4可以形成一种大的共轭体系, 使其λ_{max}由477 nm红移至545 nm.

关键词: 偶氮基杯芳烃 重氮化-偶合反应 酸效应 偶氮-醌踪互变异构

Synthesis and Azo-quinoid Tautomerism of Azocalixarene

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Abstract:

The introduction of chromophoric azo group into calixarene was of great value for the development of functional calixarenes, and the azo-coupled calixarene usually showed large UV-Vis band shifts when base was added. Eight azocalixarene compounds were synthesized by diazo-coupling reaction. These compounds were characterized by IR, ¹H NMR, ESI-MS and elemental analysis. The effect of varying pH values upon the absorption ability of both 5,11,17,23-tetra[(2-benzothiazole)azo]-25,26,27,28-tetrahydroxycalixarene and 5,17-di[(1-naphthyl)azo]-25,26,27,28-tetrahydroxycalixarene was tested to study the azo-quinoid tautomerism phenomena. Observed result exhibit that with the increasing of pH, the proportion of quinoid tautomer in azo-quinoid tautomerism equilibrium is rised. Unexpectedly an conjugated system may be formed in the condition of pH=-1 for 5,17-di[(1-naphthyl)-azo]-25,26,27,28-tetrahydroxycalixarene, of which the UV absorption spectra show substantial bathochromic shifts (Δλ=477—545 nm).

Keywords: Azocalixarene Diazo-coupling reaction Acidity effect Azo-quinoid tautomerism

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