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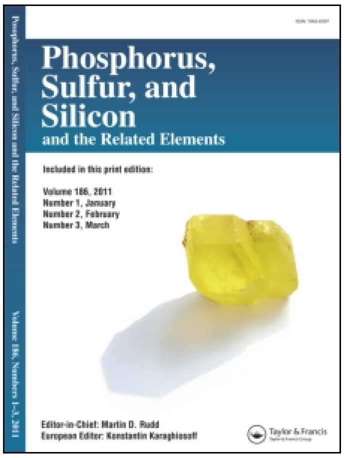

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The 2D COSY NMR Spectrum of 1,3,4,7-Tetramethyl-1-Azonia-7-Aza-6-Arsabicyclo[4.3.0]non-3-ene Tetrachlorogallate

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THE 2D COSY NMR SPECTRUM OF 1,3,4,7-TETRAMETHYL-1-AZONIA-7-AZA-6-ARSABICYCLO[4.3.0]NON-3-ENE TETRACHLOROGALLATE

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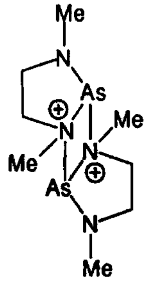
Abstract The quantitative cycloaddition product 1,3,4,7-tetramethyl-1-azonia-7-aza-6-arsabicyclo[4.3.0]non-3-ene tetrachlorogallate is characterized through the use of two-dimensional COSY NMR at 400 MHz.

Reaction of the tetrachlorogallate salt of the dimeric arsenium cation **1**[1] with a slight molar excess of 2,3-dimethyl-1,3-butadiene produces the Diels-Alder type cycloaddition product 1,3,4,7-tetramethyl-1-azonia-7-aza-6-arsabicyclo[4.3.0]non-3-ene **2** tetrachlorogallate in quantitative yield as determined by ^{1}H and ^{13}C NMR.[2] Examination of the ^{1}H NMR spectrum of the reaction mixture in CD_2Cl_2 (Figure 1) reveals a complex system which is resolvable through the use of COSY techniques at high field (400 MHz). The observed J-coupling constants and chemical shifts have allowed assignment of all proton signals. Methyl groups 1 and 2 are observed at 1.95 and 1.94 ppm, respectively. Differentiation of the two methyl groups is possible due to the long range ^5J-coupling observed to H^7 and H^5, respectively. Methyl groups 3 and 4 are observed at 3.22 [d, ^4J(Me^3, H^5) = 1.0 Hz; 3H] and 2.97 (s, 3H) ppm, respectively. The four methylene protons of the cyclopentane ring are observed in the usual region. H^1 displays a triplet of doublets at 3.15 ppm (^2J = 12.5 Hz, ^3J = 12.6 Hz, ^3J = 4.8 Hz; 1H), while H^4 exhibits a doublet of doublets of doublets at 3.90 ppm (^2J = 14.7 Hz, $^3J_{trans}$ = 12.6 Hz, $^3J_{cis}$ = 3.4 Hz; 1H). H^2 and H^3 both show a doublet of doublets at



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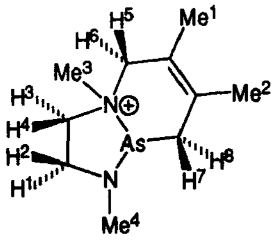

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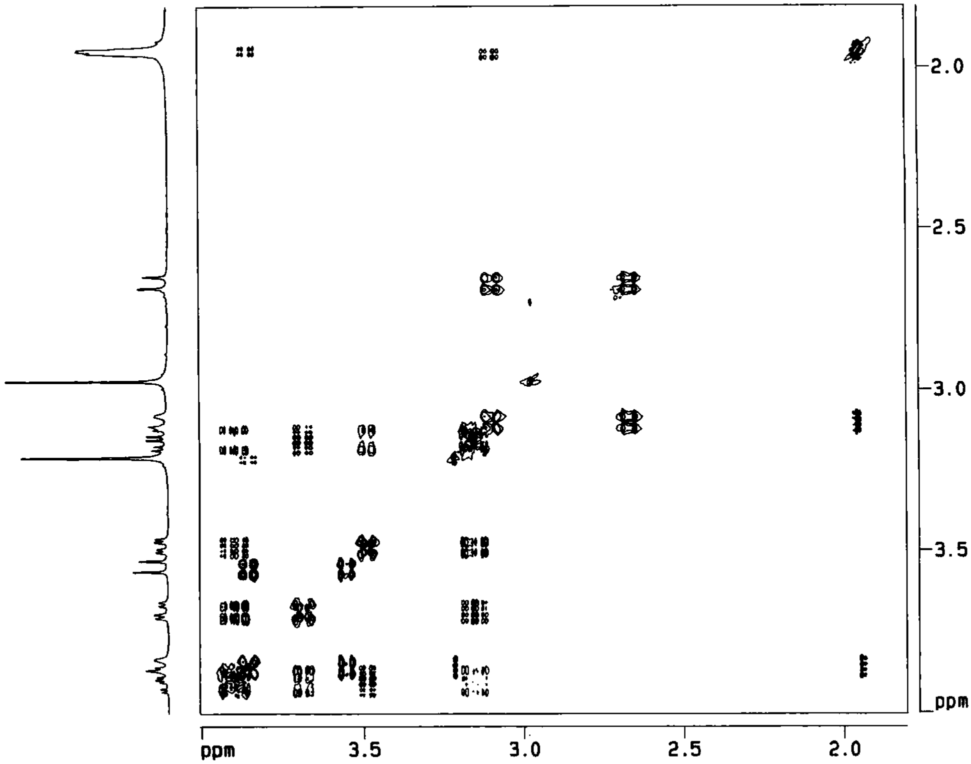

FIGURE 1 Phase-sensitive COSY NMR spectrum of **2** at 400 MHz in CD_2Cl_2 at room temperature.

3.49 ppm (^2J = 12.5 Hz, ^3J = 3.4 Hz; 1H) and 3.69 ppm (^2J = 14.7 Hz, ^3J = 4.8 Hz; 1H), respectively. The signals of H^5 and H^6 occur at 3.85 and 3.55 ppm, respectively. Both are manifest as doublets (^2J = 13.0 Hz; 1H), however H^5 is broadened as a result of long range J-coupling to Me^2 and Me^3. H^7 and H^8 show doublets at 3.10 and 2.67 ppm (^2J = 14.0 Hz; 1H), respectively, and H^7 exhibits broadening due to ^5J-coupling to Me^1 [$^5J(Me^2, H^5) \approx {}^5J(Me^1, H^7)$ = 1.7 Hz]. The observed patterns are consistent with **2** existing as the S,S and R,R diastereomers, indicating that the reaction forming **2** is stereospecific, with inversion of configuration prevented by the large pyramidal inversion barrier at arsenic.[3]

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