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ROTATIONAL ISOMERISM ABOUT SILICON-TO-CARBON SINGLE BONDS[1)]

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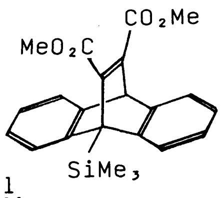
^{1}H NMR spectra of the adducts of 9-trimethylsilylanthracene with dimethyl acetylenedicarboxylate and p-quinone are temperature dependent, indicating slow rotation about silicon-to-carbon single bonds, while that of 1,4-dimethoxy-9-trimethylsilyltriptycene is indicative of completely frozen conformation with respect to the Si-C(9) bond.

Successful result that stable rotamers about a tetrahedral nitrogen-to-tetrahedral carbon single bond can be isolated at room temperature[1)] has stimulated us to investigate another atropisomerism involving a silicon-to-carbon single bond, which is longer than 1.9 Å. Recent report, which appeared during the preparation of the manuscript, on the temperature dependent spectra in a cyclotrisilane system suggesting hindered rotation about an sp^2-carbon-to-tetravalent silicon single bond has prompted us to report our results.[2)] The present communication discloses (i) dynamic behaviors of the adducts of 9-trimethylsilylanthracene with dimethyl acetylenedicarboxylate (DMAD) and p-quinone, and (ii) a supporting evidence that the rotation about the silicon-to-carbon single bond in 1,4-dimethoxy-9-trimethylsilyltriptycene is frozen in a classical sense as well as on an nmr time scale.[3)]

Diels-Alder reactions of 9-trimethylsilylanthracene[4)] with DMAD (xylene, 140 °C) and with p-quinone (acetonitrle, 80 °C) proceeded smoothly to afford the corresponding adducts **1**[5)] and **2**[6)] in quantitative and 91.5% yields, respectively. Base-catalyzed enolization of **2** followed by methylation with dimethyl sulfate provided 1,4-dimethoxy-9-trimethylsilyltriptycene (**3**) in 87.6% yield.[7)]



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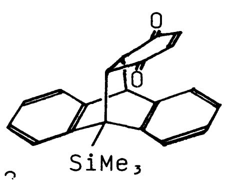

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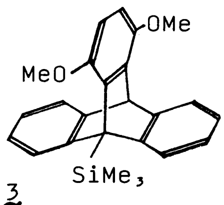

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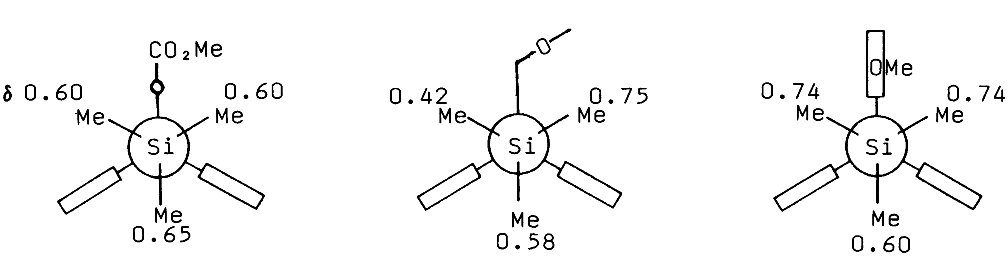

^{1}H NMR spectra of **1**, **2**, and **3** clearly demonstrate the rotational aspects of these compounds. The trimethylsilyl group of **2** gives, at an ambient temperature, a broad singlet (half-height width $w_{\frac{1}{2}}$ = 5 Hz) at 0.60 ppm, which splits into three singlets at 0.42, 0.58, and 0.75 ppm as probe temperature is lowered down to -41 °C. On the other hand, the trimethylsilyl group of **1** appears as two slightly broad singlets ($w_{\frac{1}{2}}$ = 0.9 Hz) with an intensity ratio of 2 : 1 at 0.60 and 0.65 ppm, respectively, which collapse to a singlet at higher temperatures than 70 °C. Comparison of these spectral changes with those of the calculated spectra[8] furnishes the barriers to rotation about a tetravalent silicon-to-tetrahedral carbon single bond as $\Delta G^{\ddagger}_{300}$ = 15.2$_0$ kcal/mol for **2**, and $\Delta G^{\ddagger}_{300}$ = 16.4$_9$ kcal/mol for **1**.

NMR spectral behavior of **3** is contrasted with those of **1** and **2**; the trimethylsilyl group of **3** affords two sharp singlets ($w_{\frac{1}{2}}$ = 0.7 Hz) with an intensity ratio of 1 : 2 at 0.60 and 0.74 ppm, respectively, and they remain unchanged even at 180 °C with no indication of internal rotation on an nmr time scale. This fact strongly supports that stable rotamers about an Si-C single bond can exist at room temperature. Further studies are now in progress to isolate such rotamers and to determine their rotational barriers.

References

1) Rotational Isomerism About Heteroatom-to-Carbon Single Bond II. For the preceding paper: N. Nakamura, Chem. Lett., 1982, 1611.
2) S. Masamune, Y. Hanzawa, Sh. Murakami, Th. Bally, and J. F. Blount, J. Am. Chem. Soc., 104, 1150 (1982).
3) All new compounds in the present communication gave correct elemental analyses. Mp's are not corrected. ^{1}H and ^{13}C NMR spectra were recorded on a HITACHI R-20B (60 MHz) and a Jeol FX 60 (59.85/15.04 MHz). The half-height width for TMS proton signal was 0.5-0.6 Hz.
4) C. Eaborn, R. Eidenschink, and D. R. M. Walton, J. Organomet. Chem., 96, 183 (1975); R. M. G. Roberts, ibid., 110, 281 (1976).
5) **1**: mp 66.0-67.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.60 (6H, s, Si-CH_3 x2), 0.65 (3H, s, Si-CH_3), 3.70 (3H, s, OCH_3), 3.72 (3H, s, OCH_3), 5.58 (1H, s, bridge-head H), 6.8-7.7 (8H, m, aromatic H's); ^{13}C NMR ($CDCl_3$) δ 1.03 (Si-CH_3 x2), 2.27 (Si-CH_3), 49.41 bridge-head C with Si), 51.23 (bridge-head C with H), 52.07 (OCH_3), 52.26 (OCH_3), 124.21, 124.40, 124.85, 125.37, 145.24, 145.37, 147.58, 155.50 (aromatic and olefinic C's), 164.14 (C=O), 168.49 (C=O).
6) **2**: 166.5-167.5 °C (dec); ^{1}H NMR ($CDCl_3$) δ 0.60 (9H, bs, Si-CH_3 x3), 3.14 (2H, bs, bridge-head H's originally on quinone ring), 4.71 (1H, bs, bridge-head H originally on anthracene ring), AB centered at 6.20 (2H, J = 10 Hz, δν = 14.4 Hz, olefinic H's), 6.90-7.75 (8H, m, aromatic H's); ^{13}C NMR ($CDCl_3$) δ 1.48 (Si-CH_3 x3), 43.30 (bridge-head C with Si), 49.80 (bridge-head C with H), 50.90 (quat. C α to C=O), 53.17 (quat. C α to C=O), 124.72, 125.05, 125.50, 125.76, 126.09, 126.22, 127.71, 139.99, 141.02, 141.61, 141.80, 142.91, 144.79 (olefinic and aromatic C's), 198.49 (C=O), 200.04 (C=O).
7) **3**: 261.0-262.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.60 (3H, s, Si-CH_3), 0.74 (6H, s, Si-CH_3 x2), 3.67 (3H, s, OCH_3), 3.77 (3H, s, OCH_3), 5.86 (1H, s, bridge-head H), AB centered at 6.48 (2H, J =8.5 Hz, δν = 6.2 Hz, aromatic H's), 6.75-7.75 (8H, m, aromatic H's); ^{13}C NMR ($CDCl_3$) δ 4.22 (Si-CH_3 x2), 4.83 (Si-CH_3), 46.14 (bridge-head C with Si), 47.89 (bridge-head C with H), 54.06 (OCH_3), 56.57 (OCH_3), 107.13, 109.28, 123.93, 124.38, 125.88, 128.23, 136.14, 139.03, 147.34, 148.32, 148.60, 149.05 (aromatic C's).
8) The original DNMR-3 program by G. Binsch (QCPE) was modified by Dr. Hiroshi KIHARA for the HITAC 8700 OS in the Computer Center of the University of Tokyo.

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