Barriers to Rotation of 9-Substituents in 9-Hydroxy-, 9-Amino-, and 9-Methyltriptycenes

Fumio Imashiro,* Kei Hirayama, Takehiko Terao, and A. Saika*

Contribution from the Department of Chemistry, Kyoto University, Kyoto 606, Japan.
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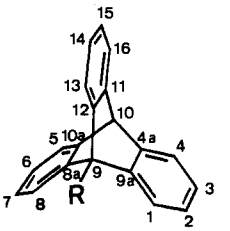
Abstract: Barriers to rotation of the 9-substituents in 9-hydroxytriptycene (**1**) and 9-aminotriptycene (**2**) are determined from the temperature dependence of proton spin-lattice relaxation times (T_1) in solids: 1.28 ± 0.05 and 2.56 ± 0.05 kcal mol^{-1} for **1** and **2**, respectively. Contributions of rotation and inversion of the amino group in **2** to T_1 are examined. The ratio of the barriers for **1**, **2**, and the 9-methyl group in 9-methyltriptycene (**3**) is 1:2.00:4.06. MM2′ molecular mechanics calculations well reproduce the barriers, showing little contribution of the torsional term in steric energies to the barriers, in contrast to the barriers to internal rotation of the corresponding methane system (methanol, methylamine, and ethane). The extra enhancement of the barrier for **3** is discussed on the basis of the MM2′ calculations.

Barriers to internal rotation in congested systems have been of experimental and theoretical interest. We obtained a value of 5.20 ± 0.13 kcal mol^{-1} for the barrier to rotation of the 9-methyl group in solid 9-methyltriptycene (**3**),[1,2] whereas molecular mechanics calculations by the MMI method[3] gave too great a value (12.07 kcal mol^{-1}) for the barrier. Subsequent experimental studies on barriers to rotation of methyl groups in several methyltriptycenes[2,4] support, however, the experimental value. Recently, we have shown that the barriers for the 9-methyl groups in methyltriptycenes are reasonably reproduced by the MM2′ method[5] with a change of the $V_3(C_{sp^2}-C_{sp^3}-C_{sp^3}-H)$ torsional parameter from 0.500 to 0.0 kcal mol^{-1}.[6]

The V_3 potentials for internal rotation in methanol (**4**),[7] methylamine (**5**),[8] and ethane (**6**)[9] (the methane system) are reported to be 1.07, 1.96, and 2.88 kcal mol^{-1}, respectively. The ratio of these values (1:1.83:2.69) is nearly proportional to the number of the protons attached to the rotating groups, indicating that the potential is, as it were, determined by additive steric interactions between the rotating group and the residual methyl group. Therefore, we investigated the barriers to rotation of the hydroxyl and the amino groups in 9-hydroxytriptycene (**1**) and 9-aminotriptycene (**2**), respectively, by proton spin-lattice relaxation times (T_1) in solids to confirm the barrier for the 9-methyl group in **3** and further to compare it with the barriers to rotation of the 9-substituents in the triptycene system. The origins of the barriers for **1-3** are interpreted in terms of steric energies on the basis of the MM2′ molecular mechanics calculations. NMR spectra for **1-3** both in solids and in solutions are also measured to examine the characteristic features of the molecular structures.

Experimental Section

Materials. 9-Hydroxytriptycene (1). By hydrolysis of 9-acetoxytriptycene, which was prepared by addition of 9-acetoxyanthracene and benzyne, with potassium hydroxide in aqueous dioxane, **1** was prepared. Recrystallization from benzene-petroleum ether gave **1** as colorless leaves, which turned to white leaves after drying at 100°C under reduced pressure: mp 245.0-246.5 °C (lit.[10] 242-243 °C).



R	
1	OH
2	NH_2
3	CH_3

9-Aminotriptycene (2). By catalytic reduction of 9-nitrotriptycene[11] employing a method similar to that by Theilacker and Beyer,[12] **2** was prepared. We used palladium carbon as a catalyst rather than platinum oxide. Recrystallization from ligroin gave **2** as white prisms: mp 223.5-224.5 °C (lit.[10] 221-221.5 °C).

NMR Measurements. ^{13}C and ^1H NMR chemical shifts for **1-3** in $CDCl_3$ solutions at room temperature were recorded on a JEOL GX-400 spectrometer operating at 100.5 and 399.8 MHz for ^{13}C and ^1H nuclei, respectively. Isotropic ^{13}C NMR chemical shifts in solids at room temperature were measured on a home-built spectrometer operating at 22.6 MHz by using the CPMAS techniques[13] with mixing times of 7-8 ms, repetition times of 3-10 s, and a sample-spinning frequency of 3.1 kHz. The sample of **1** was doped with a small amount of $CuCl_2$ to shorten the repetition time.[14] ^{13}C chemical shifts in solids were calibrated in units of ppm relative to $(CH_3)_4Si$ as described previously.[15]

Samples for T_1 measurements were degassed by several freeze-pump-thaw cycles in glass tubes. T_1 values were determined by using the home-built spectrometer operating at 90.0 MHz as described elsewhere.[1]

Results and Discussion

NMR Chemical Shifts. In Table I are collected ^{13}C and ^1H NMR chemical shifts in $CDCl_3$ solutions and ^{13}C NMR chemical shifts in solids at room temperature for **1-3**. Selective decoupling techniques were used to assign ^{13}C resonance lines of protonated carbon atoms in solutions. Delayed decoupling techniques[17] and

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Table I. ^{13}C and ^{1}H NMR Chemical Shifts for **1–3**[a]

	^{13}C						^{1}H		
	1		**2**		**3**		**1**	**2**	**3**
position	soln	solid	soln	solid	soln	solid	soln[b]	soln[c]	soln[d]
1, 8, 13	118.8	119.3	119.2	120.1	120.7	121.7	7.53	7.47	7.33
2, 7, 14	124.9	125.9	124.8	124.9	124.7	124.8	7.06	7.05	7.00
3, 6, 15	125.3	125.9	125.1	124.9	124.8	124.8	7.01	7.00	6.98
4, 5, 16	123.1	123.5	123.1	124.9	123.1	124.8	7.37	7.37	7.37
4a, 10a, 11	143.5	144.0	144.8	145.6	146.2	147.1			
9a, 8a, 12	145.7	146.1	146.5	146.8	147.0	147.1			
9	80.6	82.7	64.0	64.3	49.1	49.7			
10	52.6	54.0	53.1	54.4	53.9	56.5	5.39	5.40	5.40
CH_3, NH_2, OH					13.0	12.2	3.34	2.56	2.39

[a] Chemical shifts are given in units of ppm from $(CH_3)_4Si$. Coupling patterns appearing in ^{1}H NMR spectra are analyzed by use of the LAOCN3 program:[16] soln, values in $CDCl_3$; solid, values in solids. [b] $J_{1,2}$ = 7.7 Hz, $J_{1,3}$ = 0.9 Hz, $J_{1,4}$ = 0.1 Hz, $J_{2,3}$ = 7.4 Hz, $J_{2,4}$ = 0.8 Hz, and $J_{3,4}$ = 7.5 Hz. [c] $J_{1,2}$ = 7.5 Hz, $J_{1,3}$ = 0.5 Hz, $J_{1,4}$ = 0.0 Hz, $J_{2,3}$ = 7.4 Hz, $J_{2,4}$ = 1.2 Hz, and $J_{3,4}$ = 7.4 Hz. [d] $J_{1,2}$ = 7.5 Hz, $J_{1,3}$ = 1.2 Hz, $J_{1,4}$ = 0.4 Hz, $J_{2,3}$ = 7.5 Hz, $J_{2,4}$ = 1.4 Hz, and $J_{3,4}$ = 7.1 Hz.

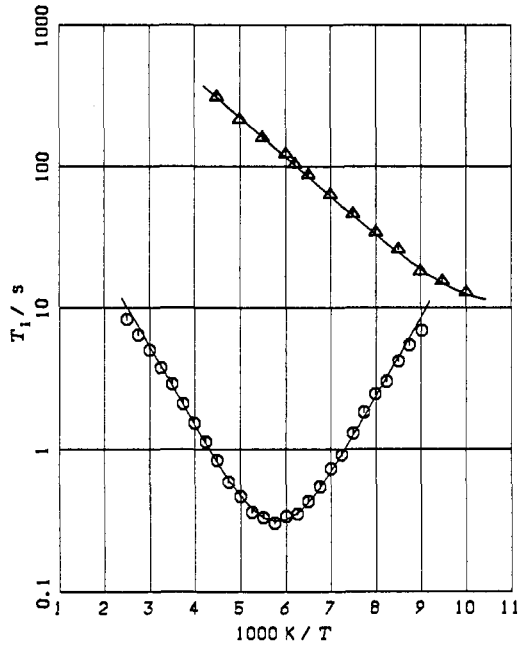

Figure 1. The temperature dependence of the ^{1}H spin-lattice relaxation times (T_1) at 90.0 MHz for 9-hydroxytriptycene (**1**: △) and 9-aminotriptycene (**2**: ○) in solids. The solid curves through the data points are "best fits" described by the parameters in Table IV.

^{13}C chemical shifts in solutions were adopted to assign ^{13}C resonance signals in solids.[18]

With increase of the bulkiness of the 9-substituents from **1** to **3**, all of the ^{13}C chemical shifts for the carbon atoms in the bicyclooctane skeleton except for the C9 carbon atom move distinctly to downfield. On the other hand, variations of the ^{13}C and ^{1}H chemical shifts of the peripheral nuclei belonging to the benzene rings are quite small except for the peri carbon and hydrogen atoms, reflecting near invariance in geometries or electronic structures of the benzene rings. Thus, molecular mechanics calculations of the triptycene system by the "mechanical aromatic ring approach"[20] may be allowed. Downfield shifts for the C9 carbon atoms are proportional to the α effect of the equatorial substituents on the ^{13}C chemical shifts in cyclohexane.[21]

Table II. "Best Fit" Parameters to the T_1 Data for **1–3**[a]

	C/s^{-2}	E_a/kcal mol^{-1}	τ_0/s
1	$(3.55 \pm 0.68) \times 10^7$	1.28 ± 0.05	$(1.0 \pm 0.2) \times 10^{-12}$
2	$(1.26 \pm 0.05) \times 10^9$	2.56 ± 0.05	$(6.2 \pm 1.0) \times 10^{-13}$
3[5]	$(1.27 \pm 0.05) \times 10^9$	5.20 ± 0.13	$(4.4 \pm 1.0) \times 10^{-13}$

[a] Error in 2.5σ (variance).

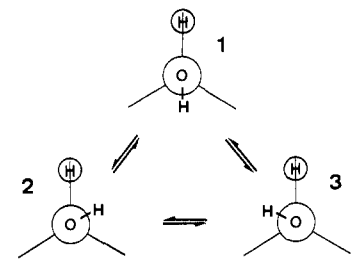

Figure 2. Rotation of the hydroxyl group in 9-hydroxytriptycene (**1**). The encircled H denotes the peri H1 hydrogen atom.

The observed trend of upfield shifts for the peri hydrogen atoms increasing from **1** to **3** is ascribed to the changes in the anisotropic deshielding effect rather than the bulkiness of the 9-substituents, while the downfield shifts for the peri carbon atoms may be affected by the δ effect of the hydrogen atoms attached to the 9-substituents.

The ^{13}C chemical shifts in solids for **1–3** are quite similar to the corresponding shifts in solutions, and extra splitting of the resonance lines is not detected in solids, indicating the three benzene rings in each molecule of **1–3** are equivalent on the NMR time scale at room temperature.

Spin–Lattice Relaxation Times, T_1. Experimental values of proton T_1 for **1** and **2** in solids are plotted against the reciprocal temperature in Figure 1. The T_1 values for **2** display a symmetric V-shaped curve with a sole minimum, while those for **1** show only a high-temperature branch of the T_1 curve. The temperature dependence of T_1 with a sole minimum is well described by the BPP (Bloembergen–Purcell–Pound) equation[22]

$$T_1^{-1} = CB(\tau) \tag{1}$$

$$B(\tau) = \frac{\tau}{1 + \omega^2\tau^2} + \frac{4\tau}{1 + 4\omega^2\tau^2} \tag{2}$$

where ω is the Larmor frequency and C is the geometrical factor. The correlation time, τ, is assumed to have an Arrhenius dependence on temperature

$$\tau = \tau_0 \exp(E_a/RT) \tag{3}$$

where E_a is the activation energy and τ_0 is the correlation time at infinite temperature. The T_1 values for **1** and **2** are fitted to

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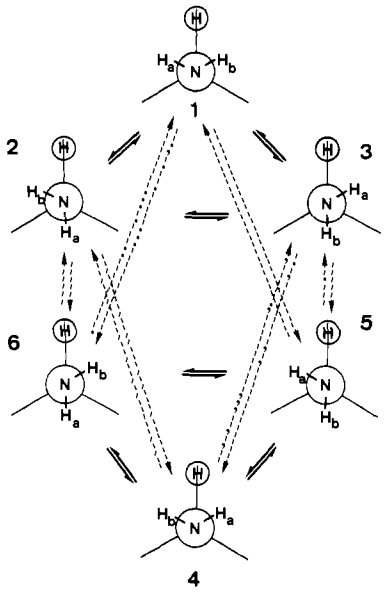

Figure 3. Rotation and inversion of the amino group in 9-aminotriptycene (**2**). Solid and broken lines represent the rotation and the inversion processes, respectively. The encircled H denotes the peri H1 hydrogen atom.

eq 1 and 2, taking C in eq 1 and E_a and τ_0 in eq 3 as adjustable parameters. The "best fit" parameters together with those for **3** obtained previously[2] are listed in Table II.

9-Hydroxytriptycene. As described in the Appendix, reorientation of the hydroxyl group in **1** shown in Figure 2 gives the same equations as eq 1 and 2 for T_1. To evaluate the geometrical factor C, we adopt the geometry generated by the MM2 molecular mechanics calculations[23,24] for **1**. C thus calculated is 1.05×10^8 s^{-2}, which is about three times larger than the experimental value. Though the factor 3 may sound very large, it would be attained by 20% lengthening of the distance between the proton pairs because of the 6th-power dependence of C on the distance. Moreover, there remain other possibilities of overestimating the C value. On the basis of the MM2 geometry for **3**, the C value due to the intramethyl dipolar interactions for the rotation of the 9-methyl group amounts to 1.44×10^9 s^{-2}. Although this value is 13% larger than the experimental one, it may be reduced by torsional oscillation of the methyl group.[25] Similar effects may also reduce the C value for **1**. Tunneling of the hydroxyl protons at low temperatures may be another reason for the observed small C value.

9-Aminotriptycene. As illustrated in Figure 3, both rotation and inversion of the amino group should be considered as the reorientation processes for **2**. T_1 for **2** should consist of two kinds of relaxation times, $(T_1)_{intra}$ and $(T_1)_{inter}$, where $(T_1)_{intra}$ denotes the contribution from the dopolar interaction between the two amino protons and $(T_1)_{inter}$ stands for the contribution from that between the amino protons and the peri hydrogen atoms

$$T_1^{-1} = (T_1)^{-1}_{intra} + (T_1)^{-1}_{inter} \quad (4)$$

As described in Appendix, $(T_1)_{intra}$ and $(T_1)_{inter}$ are functions of the combined correlation times, τ_1 and τ_3, consisting of the fundamental correlation times for the rotation (τ_R) and the inversion (τ_I)

$$(T_1)^{-1}_{intra} = C_1B(\tau_1) \quad (5)$$

$$(T_1)^{-1}_{inter} = C_2B(\tau_1) + C_3B(\tau_3) \quad (6)$$

$$\tau_1^{-1} = \tau_R^{-1} + \tau_I^{-1} \quad (7)$$

$$\tau_3^{-1} = \tau_R^{-1} + (3\tau_I)^{-1} \quad (8)$$

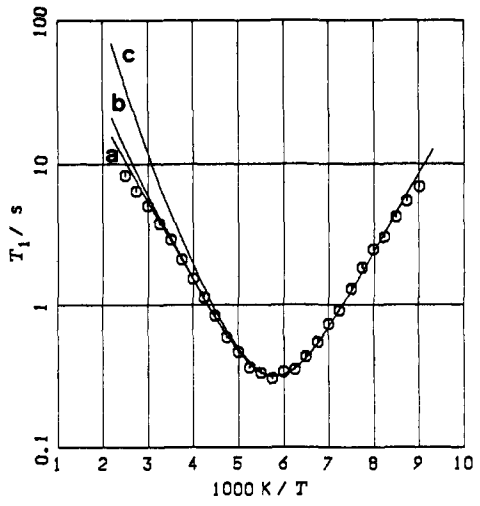

Figure 4. Variations of the proton spin-lattice relaxation times (T_1) with change of τ_0^I for 9-aminotriptycene (**2**): (a) $\tau_0^I \geq \tau_0^R$; (b) $\tau_0^I = 0.1\tau_0^R$; (c) $\tau_0^I = 0.01\tau_0^R$.

where C_1, C_2, and C_3 are the geometrical factors. τ_R and τ_I are assumed to have an Arrhenius dependence on temperature

$$\tau_R = \tau_0^R \exp(E_a^R/RT) \quad (9)$$

$$\tau_I = \tau_0^I \exp(E_a^I/RT) \quad (10)$$

where E_a^R and E_a^I are the activation energies for the rotation and the inversion, respectively, and τ_0^R and τ_0^I are the corresponding correlation times at infinite temperature. Combining eq 5 and 6, one obtains

$$T_1^{-1} = (C_1 + C_2)B(\tau_1) + C_3B(\tau_3) \quad (11)$$

From the MM2 geometry for **2**, $C_1 + C_2$ and C_3 are calculated to be 1.02×10^9 and 0.15×10^9 s^{-2}, respectively. Their sum (1.17×10^9 s^{-2}) is in good agreement with the experimental value ((1.26 ± 0.05) $\times 10^9$ s^{-2}).

Since the combined correlation times, τ_1 and τ_3, are quite similar to each other, the difference between the rotation and the inversion of the amino group in **2** should appear as different slopes of the T_1 curve with a single minimum. Therefore, we will consider why the experimental T_1 values display symmetric slopes above and below the minimum.

First, we assume that the experimental activation energy (2.56 ± 0.05 kcal mol^{-1}) is assigned to the rotation barrier of the amino group, since the value is just twice the barrier for **1**. The inversion barrier of the amino group in **2** is then assumed to be 5.4 kcal mol^{-1} on the basis of the difference (2.8 kcal mol^{-1}) between the barriers to inversion and rotation of the amino group in **5**.[26] In order to reproduce the observed T_1 minimum, $C_1 + C_2$ and C_3 are slightly increased from the calculated values to 1.10×10^9 and 0.16×10^9 s^{-2}, respectively, with the ratio for $C_1 + C_2$ to C_3 fixed. Variations of T_1 curves for different τ_0^I values are plotted in Figure 4. The slope of the T_1 curve in the high-temperature region becomes steeper with decreasing τ_0^I values. The symmetric curve is, however, obtained if τ_0^I is larger than or equal to τ_0^R. In view of small variations of τ_0 with E_a,[27] τ_0^I and τ_0^R may be considered to be similar. Consequently, we can regard the experimental activation energy for **2** as the barrier to rotation of the 9-amino group.

Barriers to Rotation of 9-Substituents. The barrier to rotation of the methyl group in **3** is much larger than that for **6**, whereas the barrier for the hydroxyl group in **1** is only slightly larger than that for **4**. The ratio of the barriers to rotation of the 9-substituents

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Table III. Steric Energies and Bond Angles by the MM2′ Method for Rotation of the 9-Substituents in **1**–**3**[a]

	1			2			3		
	TS	GS	Δ	TS	GS	Δ	TS	GS	Δ
				Steric Energy					
compression	1.29	1.09	0.20	1.55	1.13	0.42	2.25	1.33	0.92
bending	8.56	8.17	0.39	9.12	8.14	0.98	9.63	7.93	1.70
van der Waals	11.81	10.69	1.12	12.72	10.78	1.94	14.38	11.30	3.08
others[b]	−26.57	−26.83	0.26	−28.20	−28.18	−0.02	−28.40	−28.47	0.07
total	−4.91	−6.88	1.97	−4.81	−8.13	3.32	−2.14	−7.91	5.77
				Bond Angles					
C_{ar}–C9–X *A*[c]	116.2	114.7		115.6	114.5		115.7	115.1	
C_{ar}–C9–X *B*[c]	113.9	114.1		113.0	114.3		115.7	115.1	
C_{ar}–C9–X *C*[c]	2.3	0.6	1.7	2.6	0.2	2.4	0.0	0.0	0.0
C9–X–H	111.9	109.2	2.7	114.1	111.7	2.4	113.8	111.0	2.8

[a] Steric energies and bond angles are given in units of kcal mol^{-1} and deg, respectively. TS and GS denote the values in the transition and ground states, respectively, and Δ is the difference between them. X stands for O, N, or C for **1**, **2**, or **3**, respectively. [b] Including torsion, stretch–bend, and dipole-interaction terms. [c] *A* and *B* stand for the larger and the smaller values of the angles, respectively, and *C* denotes the difference between them.

for **1**, **2**, and **3** is 1:2.00:4.06, whereas the barriers are proportional to the number of the protons attached to the rotating groups in the methane system. The extra enhancement of the barrier for **3** should be ascribed to an increase in the steric interactions in the rigid triptycene skeleton.

To calculate the rotational barriers of the 9-substituents, we employ here the MM2′ molecular mechanics method using the same parameter set for aromatic carbon atoms as in the MM2 method,[23] since rotation barriers are well reproduced by the MM2′ method rather than the MM2 method. A reasonable reaction coordinate for the rotation of the amino group in **2** is obtained by simultaneously driving[28] the two torsional angles defining the angles of the two amino protons. Simultaneously driving was tried also for rotation of the 9-methyl group in **3** by the MMI method with the C_{3v} symmetry for the molecular structure of **3**.[1,2] Various steric energies and representative bond angles in the ground and transition states thus calculated for rotation of the 9-substituents are listed in Table III. The calculated barriers are 1.97, 3.32, and 5.77 kcal mol^{-1} for **1**, **2**, and **3**, respectively, which agree well with but are slightly systematically larger (by ca. 0.7 kcal mol^{-1}) than the corresponding experimental values.[29] When one recalls the small values of 0.97 and 0.00 kcal mol^{-1} for the torsional parameters $V_3(C_{sp^2}–C_{sp^3}–O–H)$ and $V_3(C_{sp^2}–C_{sp^3}–N–H)$, respectively, used in the MM2 and MM2′ methods, the revised V_3-$(C_{sp^2}–C_{sp^3}–C_{sp^3}–H)$ value[6] should be acceptable.

The main part of the barriers to rotation of the methane system is the torsional energy. The apparent additive steric interactions for the barriers follow if the values for the torsional parameters in question are similar to each other.[30] However, for the triptycene system, where the torsional energy makes only a trivial contribution, the barriers are largely due to the bending and van der Waals energies, which amount to 77, 88, and 83% for the total barriers of **1**, **2**, and **3**, respectively.[31] Both steric energies originate from the steric interactions among the 9-substituents and the peri hydrogen and carbon atoms. The extra enhancement of the barrier for **3** results, since distinct deformation of the three C_{ar}–C9–C_{Me} angles does not occur during the rotation of the methyl group (Table III). On the contrary, in the transition states of the rotation of the 9-substituents for **1** and **2**, the increased strain is reduced by nonequivalent changes of the C_{ar}–C9–O(N) angles; the nonequivalent increases of the angles are 1.7 and 2.4° for **1** and **2**, respectively, whereas the increases of the C9–X–H (X = O, N, or C) angles are very similar.

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Appendix

According to the general formulation,[32] the proton spin–lattice relaxation time T_1 is expressed by

$$\frac{1}{T_1} = \frac{9}{4}\gamma^4\hbar^2\sum_l A_l B(\tau_l) \tag{12}$$

where l stands for the normal modes of reorientation, A_l gives the effectiveness of the lth mode to the relaxation, $B(\tau_l)$ is given by eq 2, and τ_l is the correlation time of the lth mode.

To evaluate the normal modes and the effectiveness for the relaxation process in **1**, we consider dipolar interaction between the hydroxyl proton and the peri H1 hydrogen atom, where the former proton is jumping among three sites, 1, 2, and 3, shown in Figure 2, with a jumping rate of ω_R. The reorientation process is described in terms of the transition matrix D

$$D = \frac{\omega_R}{2}\begin{bmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{bmatrix} \tag{13}$$

where $-D_{ij}$ $(i \neq j)$ is the transition rate between sites i and j, and D_{ii} is the reciprocal residence time at site i. This matrix can be diagonalized by

$$U = \frac{1}{\sqrt{3}}\begin{bmatrix} 1 & 1 & 1 \\ 1 & \epsilon & \epsilon^* \\ 1 & \epsilon^* & \epsilon \end{bmatrix} \tag{14}$$

where $\epsilon = \exp(2\pi i/3)$. The diagonalized matrix Λ has only one degenerate nonzero eigenvalue

$$\Lambda_{22} = \Lambda_{33} = 3\omega_R/2 = \tau_1^{-1} \tag{15}$$

The structure-dependent coefficient A_l for the normal mode l is given by

$$A_l = \frac{2}{15}\sum_{ij}\sum_{k}{}'\sqrt{P_i^0}\sqrt{P_j^0}U_{ik}U^*_{jk}R_i^{-3}R_j^{-3}P_2(\cos\Omega_{ij}) \tag{16}$$

where the summation $\sum'_k$ is taken over k('s) of Λ_{kk}('s) with the same value as τ_l^{-1}, $P_i^0(P_j^0)$ is the equilibrium population of site $i(j)$ (here, $P_i^0 = P_j^0 = 1/3$), $R_i(R_j)$ is the internuclear distance between the protons at site $i(j)$, and Ω_{ij} designates the angle between the internuclear vectors R_i and R_j.

Consequently, T_1 for **1** is written as

(28) Wiberg, K. B.; Boyd, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 8426–8430.

(29) MM2′ calculations can reproduce the inversion barrier of ammonia with neglect of the lone-pair electrons of nitrogen and with a revised HNH bending constant (0.375 mdyn Å^{-1}), yielding 4.58 and 4.88 kcal mol^{-1} for the inversion barriers of the amino groups in **2** and **5**, respectively, without significant changes in the rotation barriers. Since the latter value is in good agreement with the experimental one,[26] the assumed value of 5.4 kcal mol^{-1} is considered as an upper limit.

(30) The V_3 parameters for H–C_{sp^3}–X–H employed in the MM2′ method are 0.200, 0.250, and 0.237 kcal mol^{-1} for X = O, N, and C_{sp^3}, respectively.

(31) A slightly smaller ratio (74%) of the bending and the van der Waals energies to the total steric energies in the methyl barrier for **3** was obtained by the MMI method.[1]

(32) (a) Soda, G. *Kagaku No Ryoiki* **1974**, *28*, 799–813. (b) Watton, A. *Phys. Rev. B* **1978**, *17*, 945–951. (c) Takeda, S.; Soda, G.; Chihara, H. *Mol. Phys.* **1982**, *47*, 501–517.

$$\frac{1}{T_1} = \frac{3}{7}\frac{\gamma^4\hbar^2}{15}B(\tau_1)\sum_{ij}(2\delta_{ij} - 1)R_i^{-3}R_j^{-3}P_2(\cos\Omega_{ij}) \quad (17)$$

where a factor 3/7 is added for intramolecular spin diffusion and δ_{ij} is Cronecker's delta.

Then we consider the relaxation for **2**, where rotation and inversion processes of the amino group should be taken into account. Figure 3 illustrates the six sites of the amino group in **2**. We assume that the rotation occurs with a single jumping rate ω_R among sites 1, 2, and 3 or sites 4, 5, and 6, and the inversion takes place with another jumping rate ω_I between sites 1 and 5, sites 1 and 6, sites 2 and 4, sites, 2 and 6, sites 3 and 4, or sites 3 and 5. The transition matrix D is given in eq 18.

$$D = \frac{1}{2} \times \begin{bmatrix} 2(\omega_R+\omega_I) & -\omega_R & -\omega_R & 0 & -\omega_I & -\omega_I \\ -\omega_R & 2(\omega_R+\omega_I) & -\omega_R & -\omega_I & 0 & -\omega_I \\ -\omega_R & -\omega_R & 2(\omega_R+\omega_I) & -\omega_I & -\omega_I & 0 \\ 0 & -\omega_I & -\omega_I & 2(\omega_R+\omega_I) & -\omega_R & -\omega_R \\ -\omega_I & 0 & -\omega_I & -\omega_R & 2(\omega_R+\omega_I) & -\omega_R \\ -\omega_I & -\omega_I & 0 & -\omega_R & -\omega_R & 2(\omega_R+\omega_I) \end{bmatrix} \quad (18)$$

This matrix can be diagonalized by

$$U = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix} \times \frac{1}{\sqrt{3}}\begin{bmatrix} 1 & 1 & 1 \\ 1 & \epsilon & \epsilon^* \\ 1 & \epsilon^* & \epsilon \end{bmatrix} \quad (19)$$

where × means a direct product. The nonzero eigenvalues of Λ are

$$\Lambda_{22} = \Lambda_{33} = 3(\omega_R + \omega_I)/2 = \tau_1^{-1} \qquad \Lambda_{44} = 2\omega_I = \tau_2^{-1}$$
$$\Lambda_{55} = \Lambda_{66} = (3\omega_R + \omega_I)/2 = \tau_3^{-1} \quad (20)$$

A_l for the normal mode l is given by eq 16 with $P_i^0 = P_j^0 = 1/6$.

After evaluation of the A_l values, one obtains the contribution of the intraamino protons to the relaxation time

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = \frac{2}{15}\frac{9}{40}\gamma^4\hbar^2 R_{HH}^{-6}B(\tau_1) \quad (21)$$

where 2/15 is a factor for the spin diffusion and R_{HH} is the distance between the amino protons. The contribution from the proton pairs between the amino protons and the peri hydrogen atoms is given by

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{4}{5}\frac{9}{4}\gamma^4\hbar^2\sum_{l=1,3}A_l B(\tau_l) \quad (22)$$

where A_2 vanishes and 4/5 is a factor for the spin diffusion.

Registry No. 1, 73597-16-7; **2**, 793-41-9; **3**, 793-39-5; 9-acetoxytriptycene, 97733-14-7; 9-acetoxyanthracene, 1499-12-3; benzyne, 462-80-6; 9-nitrotriptycene, 797-67-1.

Fundamental Studies of the Chemisorption of Organosulfur Compounds on Au(111). Implications for Molecular Self-Assembly on Gold Surfaces

Ralph G. Nuzzo,* Bernard R. Zegarski, and Lawrence H. Dubois*

Contribution from the AT&T Bell Laboratories, Murray Hill, New Jersey 07974.
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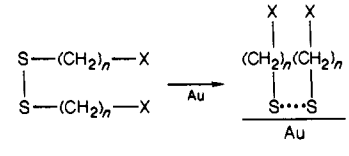
Abstract: Studies of the adsorption of methanethiol and dimethyl disulfide on an Au(111) surface under UHV conditions are described. Both adsorbates bind strongly, with the bonding of the disulfide being greatly favored. It is found that, under these conditions, the disulfide bond is dissociated to give a stable surface thiolate. Adsorption of methanethiol does not involve cleavage of the S–H bond. The implications of these results for solution adsorption experiments and the thermodynamics characterizing monolayer formation are discussed.

The adsorption of organosulfur compounds on gold surfaces represents a chemisorption system with unique and important properties. In an earlier communication,[1] a general description of the chemisorption of organic disulfides (RSSR′) from solution on clean, evaporated gold films was presented. Given the inertness of gold toward the chemisorption of most polar organic functionalities, we were surprised to find that all of the disulfides we examined formed very strong chemisorption bonds. We also observed that when an appropriate molecular structure in the adsorbate molecule is used, it is possible to prepare structurally and chemically complex organic surfaces with well-defined microscopic characteristics. Further, it was found that this technique is completely general, in that these molecular self-assembly processes (also called spontaneous organization) are disposed equally well toward the construction of both high- and low-surface free energy monolayer films.[1-6] We note that it is the preparation

Scheme I



(X = CH_3, $CHCH_2$, CO_2H, NH_2, etc.)

of high-surface free energy organic materials which most distinguishes this chemisorption system from other, well-documented films obtained by molecular self-assembly.[7-9]

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