Table I. Enantiomerization Pathways for 1

| pathway | site exchanged |
|---|---|
| zero | (aā)(bb̄)(cc̄)(dd̄)(eē)(ff̄)(gḡ)(hh̄)(ii) |
| [1] | (ab̄)(ba)(cc̄)(dd̄)(eē)(ff̄)(gḡ)(hh̄)(ii) |
| [2] | (aā)(bb̄)(cd̄)(dc)(eē)(ff̄)(gḡ)(hh̄)(ii) |
| [3] | (aā)(bb̄)(cc̄)(dd̄)(ef̄)(fe)(gḡ)(hh̄)(ii) |
| [1,2] | (ab̄)(ba)(cd̄)(dc)(eē)(ff̄)(gḡ)(hh̄)(ii) |
| [1,3] | (ab̄)(ba)(cc̄)(dd̄)(ef̄)(fe)(gḡ)(hh)(ii) |
| [2,3] | (aā)(bb̄)(cd̄)(dc)(ef̄)(fe)(gḡ)(hh̄)(ii) |
| [1,2,3] | (ab̄)(ba)(cd̄)(dc)(ef̄)(fe)(gḡ)(hh)(ii) |

enolization of related enols is slow,[1,6] and $T_c$ does not decrease appreciably in the presence of $CF_3COOH$. Moreover, the $\Delta G_c^{\ddagger}$ value for trimesitylvinyl acetate in 1,2,4-$C_6H_3Cl_3$ (19.0 ± 0.2 kcal mol$^{-1}$) is only slightly higher than for **1** (18.3 ± 0.2 kcal mol$^{-1}$). (d) Rotation around the C($sp^2$)–C(Ar) bonds—this a priori probable route is indicated by the elimination of alternatives. Direct evidence that a correlated rotation is occurring is provided by the nearly equal $\Delta G_c^{\ddagger}$ values for each ring.

On the assumption that **1** has the propeller conformation in solution,[14] Table I analyzes the eight different enantiomerization (**1a** ⇌ **1b**) routes, following Mislow's analysis of the $Ar^1Ar^2Ar^3CY$ system.[2c] Numerals in brackets indicate the flipping ring(s) in the flip routes and letters in each bracket indicate the corresponding site-exchanging groups. Successive three one-ring flips ([1], [2], [3]) or two-ring flips ([1,2], [1,3], [2,3]) or a three-ring flip ([1,2,3]) account for the coalescence results. While the three one- or two-ring flips are degenerate for trimesitylmethane, they are nondegenerate for **1** and should have different $\Delta G_c^{\ddagger}$ values. If $\Delta G_c^{\ddagger}$ is mainly determined by steric interaction of the flipping rings in the transition state,[4c] it will be higher for the [1,2] than for the [1,3] process. *Consequently, the identical* $\Delta G_c^{\ddagger}$ *values for the three rings strongly support a three-ring flip process.*[15]

β,β-Dimesityl-α-9-anthrylethenol (**2**)[8] behaves similarly: the 300-MHz $^1H$ NMR spectrum ($C_6D_5NO_2$, 290 K) shows 11 singlets [6 Me groups (δ 1.65–2.95), 1 OH group (δ 5.92), 4 mesityl-H (δ 6.11–7.07)], and 8 aromatic multiplets (δ 7.10–8.81). Pairs of diastereotopic protons or groups on the same ring were assigned by the saturation transfer technique.[9] We distinguished six different coalescence processes between 329–344 K, four for the methyl and aromatic protons of the mesityl groups [$\Delta G_c^{\ddagger}$ = 16.4 ($\Delta\nu$ = 103), 16.1 ($\Delta\nu$ = 56), 16.2 ($\Delta\nu$ = 137), and 16.2 ($\Delta\nu$ = 94.2 Hz) kcal mol$^{-1}$], and two for different pairs of the 9-anthryl ring protons [$\Delta G_c^{\ddagger}$ = 16.0 ($\Delta\nu$ = 86.4) and 16.0 ($\Delta\nu$ = 118.5 Hz) kcal mol$^{-1}$]. The identity of the $\Delta G_c^{\ddagger}$ values for the three rings definitely rule out both types of three degenerate pathways. These are the first examples where a three-ring flip in triaryl-substituted systems is strongly indicated.

The lower rotational barrier for **2** with the α-anthryl group compared with **1** finds precedent in the lower barrier for dimesityl-9-anthrylmethane compared with trimesitylmethane,[4c] where the threshold mechanism is a two-ring flip.[16]

A more extensive analysis and barriers for related enols, ketones, and enol acetates will be reported soon.

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(14) Nonpropeller conformations may also account for the data, but the X-ray data and analogy with the $Ar_3CY$ systems favors the present analysis.

(15) The zero-ring flip route which does not exchange diastereotopic groups (cf. Table I) cannot be monitored by NMR spectroscopy. In this process where the three rings pass through the reference plane the transition state is so overcrowded that it is likely that this route is of higher activation energy than the three-ring flip. A set of "nonflip" rotational mechanisms (i.e., rotation of one, two, or all three rings while the nonrotating ring remains fixed) can also lead to coalescence without helicity reversal.[4d] We tentatively exclude these routes by analogy with the behavior of the $Ar_3X$ and $Ar_3XY$ series. We plan to investigate this question by substituting our system with an appropriate enantiomerization probe.

(16) This may be fortuitous due to the different geometries and the π-(Ar)–π(C=C) interaction which may affect $\Delta G_c^{\ddagger}$ in the enols.

## Kinetics of the Reaction of *cis*-$Pt(NH_3)_2Cl_2$ with DNAs of Different G–C Content

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The fixation of *cis*-$Pt(NH_3)_2Cl_2$ (cis-PDD) to DNA appears to be the event responsible for the various biological activities of this antitumor drug,[1] but the structure of the platinum–DNA complex remains undetermined. cis-$Pt(NH_3)_2Cl_2$ itself is unreactive, but the aquated forms, *cis*-$[Pt(NH_3)_2Cl(H_2O)]^+$ and *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$, bind covalently to DNA,[2] and the overall reaction liberates two $Cl^-$.[3] Comparative studies of the reaction of *cis*-PDD and related Pt(II) compounds with nucleosides and nucleotides indicate that guanine N(7) is the kinetically preferred site of fixation[4,5] and at low $R$ ($R$ = *cis*-PDD/DNA nucleotide ratio) *cis*-PDD complexes in DNA with guanine but not with adenine.[6] Hence the initial reaction of aquated cis-PDD species with DNA seems to occur primarily if not exclusively at guanine.

The best characterized of the *cis*-$Pt(NH_3)_2$–DNA lesions is the interstrand cross-link which has been deduced from the appearance of high molecular weight DNA in denaturing conditions,[7] enhanced thermal renaturation,[8] and a diminished rate of alkaline elution.[9] However this lesion accounts for less than 1% of the platinum bound to the DNA.[10] According to X-ray crystallographic[11] and NMR solution[12] studies, guanosine forms complexes with *cis*-PDD and analogous platinum compounds in which two bases are fixed through N(7) to a single platinum atom. This type of complex has been proposed as the preferred initial binding mode of *cis*-PDD on DNA.[13] Alternatively, chelation on a single guanine at N(7)–O(6)[3,14-16] or N(1)–O(6)[17] has also been suggested.

The purpose of the present experiment was to test the hypothesis that *cis*-PDD binds preferentially to G–G sequences of DNA.[13] We have measured the kinetics of the reaction of aquated *cis*-PDD with equal concentrations of DNAs from *Micrococcus lysodeikticus* (35% G)[18] and *Clostridium perfringens* (15.8% G)[18] at $R$ less than $10^{-3}$. Fixation of aquated *cis*-PDD on DNA is first order with respect to the concentration of DNA binding sites.[2] If *cis*-PDD reacts at all guanine bases with equal probability, then the rate of reaction should be two times greater for *M. lysodeikticus* DNA. If, on the other hand, the compound reacts either simultaneously or stepwise at G–G sequences, then the reaction rate will be proportional to the relative frequency of G–G nearest

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Table I. Apparent Rates of Reaction of *cis*-$[Pt(NH_3)_2Cl(H_2O)]^+$ with Two DNAs Compared with the Frequency of Occurrence of G and G–G[18]

| | *M. lysodeikticus* | *Cl. perfringens* | *M.l./Cl.p.* |
|---|---|---|---|
| reaction rate (–% free Pt/s) | 0.027 ± 0.007 | 0.016 ± 0.002 | 1.7 ± 0.7 |
| G | 0.35 | 0.158 | 2.2 |
| G–G | 0.112 | 0.026 | 4.3 |

neighbors[18] and should differ by a factor of 4 (Table I).

An aqueous 0.6 mg/mL solution of *cis*-$Pt(NH_3)_2Cl_2$ (prepared from $K_2[PtCl_4]$[19]) was equilibrated for 10 days in the dark at room temperature in order to form the reactive species[2] *cis*-$[Pt(NH_3)_2Cl(H_2O)]^+$ and *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$. At zero time a portion of this solution was added to a 0.250-mg/mL solution of *M. lysodeikticus* or *Cl. perfringens* DNA (Sigma) at an *R* of 0.006 in $10^{-2}$ M $NaClO_4$ (Fluka) at 37 °C, pH 5.5–6.0. Aliquots of 0.2 mL were removed every 30 s, added to 0.1 mL of ice-cold 0.9 M sodium acetate (Prolabo), vortexed, mixed with three volumes of ice-cold ethanol (Prolabo), and frozen at −40 °C to precipitate the DNA. The precipitate was centrifuged for 5 min at 12 000 rpm, resuspended in 0.3 mL of 0.3 M sodium acetate, precipitated as above, and centrifuged. The pellet was washed with ethanol, dried under vacuum, resuspended in 0.5 mL of 10 mM $NaClO_4$, and agitated for 2 days at room temp. to dissolve the DNA. Control experiments in which the reaction with DNA was blocked by the addition of 0.1 M NACl showed that all unreacted platinum was removed from the DNA by this method of precipitation and washing. The concentration of the double-stranded DNA in each aliquot was determined by UV spectrophotometry with a Zeiss PMQII assuming that 10 μg/mL corresponds to $A_{260}$ = 0.210. The platinum concentration was measured by using a Perkin Elmer Atomic Absorption Spectrophotometer Model 603 equipped with a graphite furnace, and the percent unreacted platinum in each aliquot was calculated from the measured *R* bound.

The data in Figure 1 show the change in concentration of unreacted platinum as a function of time for three separate experiments with each DNA. Kinetics were not measured for the fixation of the first 3 platinum per $10^4$ nucleotides which bound in a few seconds as a result of the fast reaction[2] with *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$. It was more difficult to dissolve the precipitated *M. lysodeikticus* DNA than the *Cl. perfringens* DNA which may account for the greater uncertainty of DNA binding in the first case. The data in each experiment were distributed randomly around the best straight line fit as determined by linear regression. Apparent reaction rates (–% free Pt/s) were determined from the slope of this line (Table I).

The ratio of the initial rates of binding shown in Table I was 1.7 ± 0.7 which corresponds to the relative number of guanines in each polynucleotide. Table I also shows the frequency of G–G nearest neighbors in the two DNAs.[18] If the platinum bound exlusively to two adjacent guanines (either bidentate chelation on two neighboring Gs or initial monodentate fixation at one G followed by a slower reaction with the adjacent G), then the rate of the reaction should be 4.3 times greater for *M. lysodeikticus* DNA. Since this value is greater than 3 standard deviations from the observed ratio, the probability that the data in Figure 1 originates from random fluctuations in reactions whose rates differ by a factor of 4.3 is about $10^{-3}$.

In conclusion, if aquated *cis*-PDD initially reacts with DNA at guanine then the simplest interpretation of our results would be that, in vitro, Pt is fixed at all guanine bases with equal probability. Hence the number of *cis*-PDD bound to adjacent guanines can be no greater than the likelihood of finding a guanine base on one side or the other of the initial site of fixation. This can be estimated as 2P(G) – P(G)·P(G) where P(G) is the percent guanine in the DNA. In vitro binding of a single *cis*-$Pt(NH_3)_2$- to neighboring guanine bases should occur for no more than 58% of the Pt fixed to *M. lysodeikticus* DNA and 29% of the Pt fixed to *Cl. perfringens* DNA.

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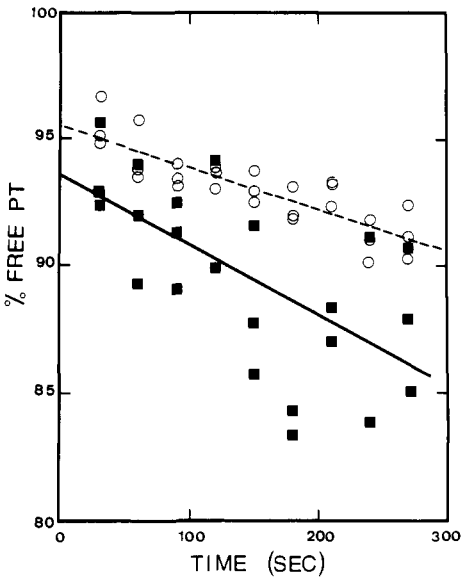


**Figure 1.** Percent unreacted platinum as a function of time of reaction at 37 °C with *Cl. perfringens* (○) and *M. lysodeikticus* (■) DNA; 0.006 Pt/DNA nucleotide initial molar ratio.

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## Phenylmethylpolysilanes: Formable Silane Copolymers with Potential Semiconducting Properties

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Although silane polymers were apparently obtained by Kipping more than 50 years ago,[1] and permethylpolysilane was prepared as early as 1949,[2] the chemistry of the polymeric polysilanes has been neglected until recently. Yajima and Hayashi's demonstration that permethylpolysilane can be converted in a two-step process to β-SiC fibers[3] has led to a resurgence of interest in these materials.[4–6]

Permethylpolysilane is known only as a highly crystalline intractable solid. In 1978 we reported the use of meltable, partially crystalline silane–dimethylsilane copolymers with dimethyl/phenylmethyl ($Me_2Si$/PhMeSi) ratios of from 10/1 to 3/1 as impregnating agents for strengthening silicon nitride ceramics.[7] The ceramic body is soaked in a melt of the polymer and then fired, leading to formation of β-SiC threads in the pore spaces with consequent strengthening of the ceramic.

We now find that crystallinity is greatly reduced at lower $Me_2Si$/PhMeSi ratios, with a minimum near the molar ratio 1/1.

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