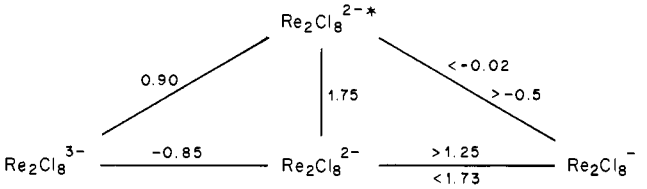
a modified Latimer diagram (excited-state energy in eV; electrode potentials vs. SCE in CH_3CN solution):



The $Re_2Cl_8^{2-*/3-}$ reduction potential of 0.90 V vs. SCE is consistent with the relatively low k_q values measured for quenchers 5–9 (Table I). The corresponding value for $Re_2Cl_8^{-/2-*}$ is not well determined, because the electrochemical oxidation of $Re_2Cl_8^{2-}$ to $Re_2Cl_8^{-}$ is not reversible. The estimated upper limit [$E°(Re_2Cl_8^{-/2-*}$ <–0.02 V vs. SCE) is based on our finding that chloranil is an efficient quencher.[12] This in turn places an upper limit of 1.73 V vs. SCE on the $Re_2Cl_8^{-/2-}$ reduction potential in acetonitrile solution.

The rich redox chemistry of $Re_2Cl_8^{2-*}$ is potentially exploitable for photochemical energy storage applications. In this connection we emphasize that the $\delta\delta^*$ singlet provides a facile route to an extremely powerful inorganic oxidant, $Re_2Cl_8^{-}$, a species that has not been generated cleanly by other means. The goal of experiments now in progress in our laboratory is to elucidate the chemistry of various photogenerated octachlorodirhenates (2–*, –, 3–) in aqueous solution.

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(11) Cyclic voltammetric measurements; our value of –0.85 V vs. SCE for $E_{1/2}(Re_2Cl_8^{2-/3-})$ in acetonitrile solution ($[(Bu_4N)_2Re_2Cl_8]$ = 1 × 10^{-3} M, [TBAP] = 0.1 M, 25 °C) accords closely with the results of earlier electrochemical experiments (Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 383–387).

(12) For chloranil/chloranil$^-$ in acetonitrile solution (25 °C), $E_{1/2}$ = –0.02 V vs. SCE (Peover, M. E. *Nature (London)* **1961**, *191*, 702–703).

Stable Simple Enols. 2.[1] Correlated Rotation in Two β,β-Dimesityl-α-arylethenols. A Probable Example of a Three-Ring Flip

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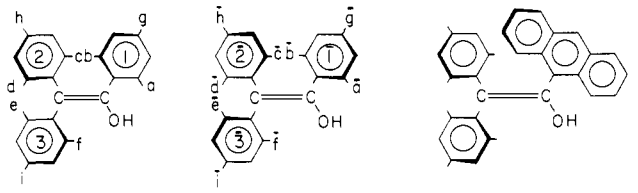
Molecular propellers of the form Ar_3X and Ar_3XY (X = C, B, N) show correlated rotation.[2b,c] Four different rotational modes[2] which lead to helicity reversal involve zero-, one-, two-, and three-ring flips. In the zero- and three-ring flips all three rings rotate in the same direction; in the one- and two-ring flips, two rings rotate in one direction and the third rotates in the opposite direction.[3] It has been established that the rotational mode of lowest activation energy is the two-ring flip.[4]

The triarylvinyl system $Ar^3Ar^2C{=}C(Y)Ar^1$ is the vinyl "propeller" analogue of $Ar^1Ar^2Ar^3CY$. Because of the presence of the double bond there are additional potential routes and less degeneracy of the flipping routes, leading to enantiomerization and a larger maximum number of stereoisomers. To our knowledge, these routes have not been studied or analyzed previously.

Several triarylethenols are stable in the enol form.[5] In a continuation of our studies of their properties,[1,6] the ^1H NMR spectra and internal rotation of several enols were studied. Most investigated was trimesitylethenol (**1**)[5c] which by X-ray diffraction is a distorted molecular propeller[7] capable of existing as enantiomeric right- or left-handed forms **1a** and **1b** (letters with an overbar indicate enantiomeric sites). All the six *o*-methyl groups,



1a 1b 2

the three *p*-methyl groups, and the six aromatic protons of each enantiomer are diastereotopic. The 300-MHz ^1H NMR spectrum ($C_6D_5NO_2$, 298 K) shows 16 separate singlets, 9 methyl groups (δ 1.84–2.68), 1 OH group (δ 5.46), and 6 aromatic protons (δ 6.39–6.98).

NMR signals were assigned by isotopic labeling of the methyl groups of the β rings and by synthesis of β-*p*-*tert*-butyl- and α-2,6-dimethylphenyl analogues.[8] The saturation transfer technique[9] was valuable for identifying unequivocally the coalescing protons on each ring. Irradiation of one *o*-Me (or Ar–H) signal to saturation caused an intensity diminution of another *o*-Me (or Ar–H) peak and vice versa, indicating pairs of protons which are involved in a dynamic exchange process.[9]

Upon raising the temperature the three pairs of *o*-methyl groups and the three pairs of aromatic protons coalesce. We measured four coalescence temperatures (T_c) with practically identical ΔG_c^* values: 18.1 (Ar–H in a β ring; $\Delta\nu$ = 16 Hz) and 18.4 (c → d or e → f; $\Delta\nu$ = 10 Hz) kcal mol^{-1} at 352 K and 18.2 (c → d or e → f; $\Delta\nu$ = 84 Hz), and 18.4 (a → b; $\Delta\nu$ = 61 Hz) kcal mol^{-1} at 376 K.[10]

Four different dynamic processes may account for the coalescence. (a) Rotation around the double bond—this has precedents[11] but is excluded since the *p*-methyls (h, i) of the β rings do not coalesce. (b) Reversible S_N1 ionization of the OH group to form a vinyl cation—this is unlikely due to the low nucleofugality of the OH group and the slowness of vinylic solvolysis.[12,13] (c) Ketonization followed by enolization—this is excluded since trimesitylethanone cannot be prepared,[5c] the CF_3COOH-catalyzed

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(3) A "flip" is a passage through a plane perpendicular to the reference plane with no edge interchange. The nonflipping rings pass through the reference plane with edge interchange.

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(13) With good nucleofuges, this route should be considered together with possible degenerate rearrangements across the double bond of the intermediate ion.[12]

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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]	(aa)(bb̄)(cd̄)(dc)(eē)(ff̄)(gḡ)(hh̄)(ii)
[3]	(aa)(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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