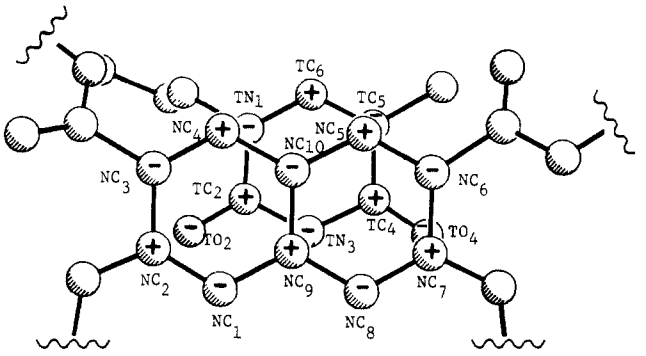
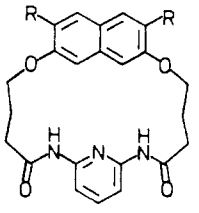
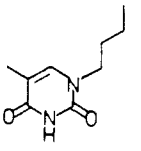


Figure 2. Top view of aromatic-aromatic interaction in **4**:**6** with electronic charge distributions (sign only) superimposed.

ration of different substituents into the naphthalene-3,6-positions in the basic receptor **3** allows us to vary the electronic charac-





6

3, R = H
4, R = $CO_2(CH_2)_2CH_3$
5, R = $O(CH_2)_3CH_3$

teristics of the stacking unit and assess its effect on the binding geometry. For example, diester macrocycle **4**[6] forms a strong complex with 1-butylthymine **6** (K_s = 570 M^{-1}, $-\Delta G°$ = 3.75 kcal mol^{-1})[7] in $CDCl_3$. Selective upfield shifts in the thymine CH and CH_3 ^1H NMR resonances (0.17 and 0.16 ppm) suggest a face-to-face geometry for the complex and this is confirmed by X-ray crystallography (Figure 1a). The naphthalene is positioned directly above and almost parallel to the pyrimidine at an interplanar distance of 3.54 Å. An insight into the origins of the special stabilization from stacking can be gained from MNDO calculations on 2,7-dimethoxynaphthalene-3,6-dicarboxylic acid (N) and thymine (T).[9,10] The resulting electronic charge distributions on the two planes are superimposed (sign only) on a downward view of **4**:**6** in Figure 2. This shows a precise alignment of *five* pairs of oppositely charged atoms (NC_2TO_2, NC_4TN_1, NC_5TC_5, NC_7TO_4, NC_9TN_3) confirming the importance of complementary electrostatic interactions in parallel stacking.[11]

Similar MNDO calculations[9] on 2,3,6,7-tetramethoxynaphthalene predict a reversal of sign at NC_3, NC_4, NC_5, and NC_6 and a diminution of charge at NC_9 and NC_{10}. Thus, in a face-to-face geometry with thymine (as in Figure 2) there would be repulsive electrostatic interactions between NC_4–TN_1 and NC_5–TC_5. To investigate this effect tetraether macrocycle **5** was prepared[6] and shown to bind 1-butylthymine **6** more weakly (K_s = 138, $-\Delta G°$ 2.92 kcal mol^{-1})[7] than either diester **4** or unsubstituted **3**.[5a,7] The absence of upfield shifts of the thymine CH and CH_3 resonances in the ^1H NMR of complex **5**:**6** argues against a parallel stacked geometry, whereas selective upfield shifts of the naphthalene-1,8-protons (0.13 ppm) suggest a solution conformation for **5**:**6** in which the 1,8-edge of the naphthalene is closer to the H-bonding plane than the 4,5-edge. Additional support for such an orientation comes from the crystal structure of complex **5**:**6** (Figure 1b) which shows the naphthalene to be almost perpendicular (77°) to the thymine–pyridine plane.[12] Furthermore, the naphthalene-1,8-protons project toward the region of negative charge formed by TO_2, TO_4, and TN_3 at distances of 2.69 and 2.24 Å from its mean plane. This edge-to-face interaction seems to be favorable as it provides a small stabilization (0.26 kcal mol^{-1}) for the complex compared to acyclic 2,6-dibutyramidopyridine.[5a,7]

Within a simple series of thymine receptors we have demonstrated that the geometry of aromatic–aromatic interactions in molecular recognition can be controlled by modifying the electronic characteristics of one component. Notably, an electrostatic complementarity between partial charges on the rings can lead to strong face-to-face stacking, while in the absence of such effects a weaker edge-to-face interaction is preferred.

Acknowledgment. We thank the National Institutes of Health (GM 35208) for partial support of this work.

Supplementary Material Available: Crystallographic details for **4**:**6** and **5**:**6** including tables of atomic coordinates, thermal parameters, bond angles, and bond lengths (20 pages). Ordering information is given on any current masthead page.

(6) Details of the synthesis and spectroscopic properties of macrocycles **5** and **6** will be reported in full later.

(7) Determined by Foster–Fife[8] analysis of ^1H NMR titration data at 25 °C. For example, in the titration of **4** and **6** the concentration of **6** was 0–9.0 × 10^{-2} M, the maximum observed shift (at 10 equiv of **6**) of the **4**-amideNHs was 2.86 ppm, and the saturation shift was calculated[8] to be 2.92 ppm. Values for **3** and **6** are K_s = 290 M^{-1}, $-\Delta G°$ = 3.36 kcal mol^{-1} and for 2,6-dibutyramidopyridine and **6** K_s = 90 M^{-1}, $-\Delta G°$ = 2.71 kcal mol^{-1}.[5a]

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(12) For other examples of edge-to-face orientations in macrocyclic chemistry see: Anelli, P. L.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *Tetrahedron Lett.* **1988**, 1575 and references therein.

σ Delocalization Induced Stereoselectivity in the Capture of Cumyl Cations and Failure of Stabilizing Substituents To Suppress It

M.-H. Lin, C. K. Cheung, and W. J. le Noble*

Department of Chemistry, State University of New York Stony Brook, New York 11794

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One of the few questions not adequately addressed in the years of controversy about the solvolysis of 2-norbornyl derivatives[1] is whether a stabilizing α-substituent can "swamp" σ participation. The assumption that it can and would is the cornerstone of the position that such assistance is not important in determining epimeric rate ratios in solvolysis. The origin of this premise appears to be the elegant demonstration by Gassman and Fentiman[2] that α-substituents such as *p*-anisyl reduce anti/syn ratios of formation and capture of the 7-norbornenyl cation from ten million nearly to unity, thus justifying their conclusion that π participation occurs and that donating substituents can suppress it. Its extension to σ participation has only rarely been questioned,[3] and, indeed, the observation of many equilibrating pairs of tertiary 2-norbornyl ions demands that α delocalization in those cases cannot be strong enough in the fully developed ions to prevent distortion from C_{2v} symmetry. It is unfortunate that the phrase "equilibrating ions" has become virtually synonymous with "unassisted solvolysis", because such usage implies a criterion that may not be justified: the operation of swamping of σ participation has only been *assumed*.

We recently reported[4] *Z*/*E* ratios for the capture of nucleophiles by several tertiary 5-substituted adamant-2-yl cations and ada-

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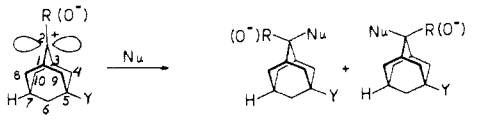
mantan-2-ones under conditions of kinetic control. The important features of these reactions are the following. First, in spite of the near C_{2v} symmetry of the system, the capture ratios depart sig-



nificantly from unity. Secondly, syn approach is favored when Y is a powerful electron acceptor such as fluoro or *p*-nitrophenyl, and anti approach is preferred when Y is *p*-anilino. Finally, since steric effects or solvent-separated ion pairs do not qualify as explanations for these facts, the only alternative available is σ delocalization. Thus, 5-fluoro substitution diminishes the ability of the C_3–C_4 and C_1–C_9 bonds to participate in comparison with the otherwise equivalent bonds C_3–C_{10} and C_1–C_8, resulting in the observed stereochemistry.

In the previous experiments, the range of groups R was not very wide, including only methyl, propargyl, and hydrogen. We now find that nucleophiles capture 5-fluoroadamant-2-yl cations with almost undiminished preference for *Z* approach even with 2-phenyl substitution. Cumyl cations have long occupied a central position in organic chemistry, as the basis of the σ^+ constants;[5] this report is the first instance of stereoselectivity in the capture of such ions in the absence of possible steric influences.

Treatment[6] of either *E* or *Z* para substituted cumyl alcohol (R = Ph, Nu = OH) with tosyl chloride gave a completely equilibrated mixture of *E*- and *Z*-tosylates in every case as judged by ^{13}C NMR. Addition of these mixtures to basic aqueous glyme solutions of sodium borohydride[7] led to reduction products that were separated by means of flash chromatography. The pure hydrocarbons were used to assign[8] the ^{13}C NMR resonances; the crude mixtures were used for analysis, which was based on the C_2 resonances. With *p*-MeO, *p*-Me, and *p*-H the *E*/*Z* ratios were 78/22, 74/26, and 75/25, respectively: the swamping associated with *p*-anisyl was not observed.

The yields with the *p*-Br and *p*-CF_3 analogues were too low to give meaningful information; accordingly, we tried the reaction of HCl with the corresponding alcohols in dry methylene chloride.[9] In this instance, the *Z*/*E* ratios with *p*-CF_3, *p*-Br, *p*-H were 77/23, 76/24, and 73/27, respectively; clearly, increased electron demand did not lead to a significant change in the ratio either (extension to more donating substituents was not feasible because the product chlorides begin to equilibrate).

Possibly even more informative is the borohydride reduction of the 2-methoxy-5-fluoroadamant-2-yl cation, produced from the dimethylketal and BF_3 etherate and isolated as the solid salt. This experiment, reminiscent of one carried out by Traylor and Perrin,[10] gave the *E*- and *Z*-methyl ethers in an 83:17 ratio; thus, not even a methoxy group directly bound to the carbocation center can quench the σ delocalization induced tendency toward syn approach. Finally, when 5-fluoroadamantan-2-one is treated with para-substituted phenylmagnesium bromides, the cumyl alcohols are also once again formed with a uniform and clear prejudice (also about 70/30) for the *E* product (hence, syn approach).[11]

It is concluded that σ delocalization cannot be swamped by means of donating substituents at the electron deficient center. Whether such delocalization should be called σ participation (which is held to produce nonclassical distortions) or hyperconjugation (which Brown[1] *considers* as not doing so), the important point is that the failure of stabilizing 2-substituents in the 2-adamantyl cation to suppress it invalidates the assumption of swamping in the 2-norbornyl ion as well.[12] The recent observations of equilibrating 2,5-dimethyladamant-2-yl cations by Sorensen[13] and Laube's X-ray study[14] of the $SbCl_5$ complex of 5-phenyladamantan-2-one offer powerful indications that at least some distortion of the adamantane structure occurs.[15]

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(14) Laube, T.; Stilz, H. U. *J. Am. Chem. Soc.* **1987**, *109*, 5876.
(15) We take note here of the fact that Grob has confirmed our observations[4a] of the unexpectedly powerful 5-substituent effect on the rates of formation and capture of the 2-adamantyl cation; however, he writes that our conclusion of σ delocalization or hyperconjugation "conflicts with the observed lower inductivity of the γ carbon C_4 compared to that of the δ carbon C_5". Apparently Grob overlooked the fact that C_5 substituents deactive *both* C_1–C_9 *and* C_3–C_4 bonds, whereas a C_4 substituent leaves the C_1–C_9 bond essentially unaffected (see: Grob, C. A.; Wang, G.; Yang, X. *Tetrahedron Lett.* **1987**, *28*, 1247).

Unbridged and Bridged Isomers of $W_2(PCy_2)_2(NMe_2)_4$: Preparations, Characterizations, and Comments on Thermodynamic and Activation Parameters for the Closing of Phosphido Bridges in d^3–d^3 Dinuclear Compounds

William E. Buhro,[1] Malcolm H. Chisholm,* Kirsten Folting, John C. Huffman, James D. Martin, and William E. Streib

Department of Chemistry and Molecular Structure Center Indiana University, Bloomington, Indiana 47405

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We describe herein the preparation and structural characterization of unbridged and bridged isomers of formula $W_2(PCy_2)_2(NMe_2)_4$ where Cy = cyclohexyl.[2] This is the first isolated example of both unbridged and bridged *isomers* of a phosphido metal complex,[3] and the first example of unbridged and bridged *isomers* of $M_2Y_2X_4$ d^3–d^3 dimers.[2] Dinuclear phosphido complexes having PR_2 groups in terminal positions are rare and typically very reactive.[3,4] Our terminal isomers are likely stabilized kinetically by steric congestion and thermodynamically by strong M–M triple bonds. Phosphido ligands are ubiquitous bridging groups, and our results provide the first information regarding the energetics of phosphido bridge formation.

The reaction between 1,2-$W_2Cl_2(NMe_2)_4$[5] and $LiPCy_2$ (2 equiv) proceeds in tetrahydrofuran (−78 to 0 °C) to give 1,2-$W_2(PCy_2)_2(NMe_2)_4$. The orange crystalline compound *gauche*-1,2-$W_2(PCy_2)_2(NMe_2)_4$ was obtained by crystallization from

(1) Chester Davis Fellow, 1985/1986. Present address: Department of Chemistry, Washington University, St. Louis, MO 63130.
(2) (a) Unbridged compounds of the type $X_2YM{\equiv}MX_2Y$ where M = Mo and W are now well known: Chisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 21. (b) The first example of a bridged $X_4M_2(\mu\text{-}Y)_2$ compound, $(t\text{-}BuO)_4W_2(\mu\text{-}PPh_2)_2$, was recently reported: Buhro, W. E.; Chisholm, M. H.; Folting, K.; Eichhorn, B. W.; Huffmann, J. C. *J. Chem. Soc., Chem. Commun.* **1987**, 845.
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