

providing a sample of natural aphidicolin, and Professor E. J. Corey for providing spectra of synthetic **16** and **17**. We are especially grateful to Chris Lovett and Owl Technical Associates, Inc., for their generous loan of a Thorn polarimeter.

Hydrogen Transfer from 1-Naphthol Triplet to Ground-State Benzophenone: Kinetic Evidence against Proposed Exciplex Intermediacy

A. A. Gorman,* I. Hamblett, C. Lambert, and R. C. Potter

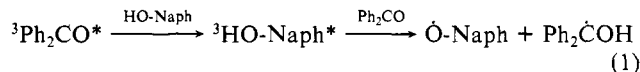
Department of Chemistry, University of Manchester
Manchester M13 9PL, U.K.

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A recent report by Shizuka et al.¹ concerns the transfer of hydrogen from the triplet state of 1-naphthol to the ground state of benzophenone in methanol. Production of the naphthol triplet was by energy transfer from triplet benzophenone, itself formed by pulsed nitrogen laser excitation at 337 nm. The critical mechanistic conclusion of this work was that the H-transfer process takes place within a triplet exciplex, cf. Scheme 1. This conclusion was based on curvature observed in plots of the first-order constant for naphthol triplet decay, k' , as a function of benzophenone concentration [(1–14) $\times 10^{-3}$ mol L⁻¹]. No changes in the absorption characteristics of the naphthol triplet were noted either with time or ketone concentration. This was attributed to lack of π - π interaction within the exciplex, possibly due to H-bonding-induced association as depicted in Scheme 1. Given the assumption of this scheme, standard exciplex kinetic treatments and curve-fitting routines were employed to define rate and activation parameters for the system, an equilibrium constant for exciplex formation of 14.1 L mol⁻¹ at 300 K being determined.

We have also examined the 1-naphthol/benzophenone system, albeit in benzene using the pulse radiolysis technique,² and have found no evidence for exciplex intermediacy. However, since extrapolation from one medium to another, particularly from aprotic to protic, is clearly not possible, we have carried out experiments essentially identical with those reported by Shizuka et al.; again we find no evidence whatsoever for exciplex intermediacy.

Thus, deaerated methanol solutions of 1-naphthol (3×10^{-3} mol L⁻¹) containing various benzophenone concentrations [(3–30) $\times 10^{-3}$ mol L⁻¹] were subjected to excitation with the third harmonic (355 nm; 12 ns) of a Q-switched Nd:YAG laser. Transient absorption spectroscopy was in excellent agreement with the overall sequence proposed by Shizuka et al., eq 1. Formation



of the naphthol triplet (λ_{max} 430 nm) by energy transfer from triplet benzophenone (λ_{max} 525 nm) was essentially complete within 400 ns. Subsequent reaction with ground-state benzophenone gave the corresponding ketyl (λ_{max} 550 nm) and naphthyloxy (λ_{max} 390 nm) radicals, cf. spectra reproduced in Figure 1a. It is clear from these spectra that the radicals exhibit significant absorption at 430 nm, the naphthol triplet maximum. This is confirmed by the decay of transient absorption at 430 nm reproduced in Figure 1b which shows "fast" decay of triplet and "slow" decay of radicals. It is therefore clear that determination of the first-order constant for decay, k' , of naphthol triplet as a function of benzophenone concentration, the relationship leading Shizuka et al. to propose exciplex intermediacy, is a nontrivial exercise. Radical decay is kinetically second order. We have therefore analyzed the decay of transient absorption at 430 nm

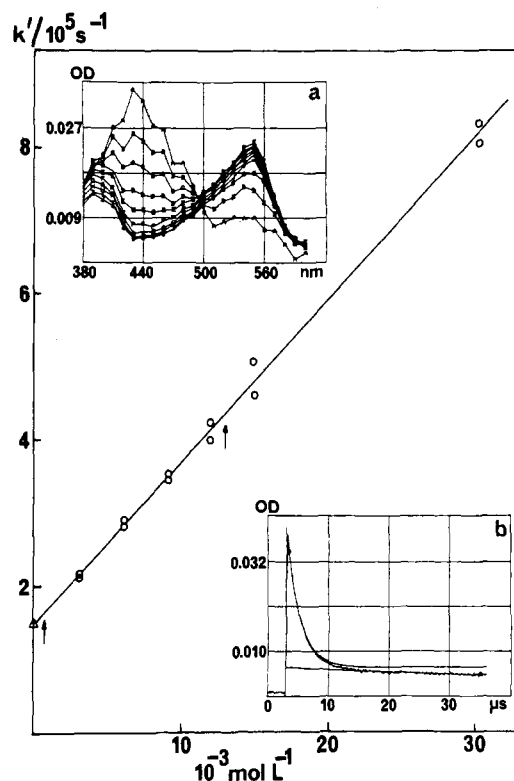
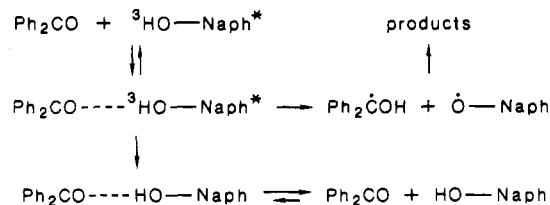


Figure 1. First-order constant, k' , for 1-naphthol triplet decay at 298 K, determined at 430 nm, as a function of benzophenone concentration; the data point at zero concentration corresponds to the intercept obtained by Shizuka et al.¹ at 300 K. Insets: (a) transient absorption spectra measured 0.4 (A), 1.0 (B), 1.7 (C), 2.7 (D), 3.7 (E), 5.5 (F), 7.5 (G), 9.5 (H), 11.5 (I), and 13.5 (J) μ s after absorption of a 12-ns laser pulse (355 nm) by deaerated methanol containing 1-naphthol (3×10^{-3} mol L⁻¹) and benzophenone (1.51×10^{-2} mol L⁻¹); (b) decay of transient absorption at 430 nm for a similar experiment with 1-naphthol (3×10^{-3} mol L⁻¹) and benzophenone (1.21×10^{-2} mol L⁻¹) showing fit for independent first-order (fast) and second-order (slow) processes together with individual components.

Scheme 1



as a combination of independent first- and second-order processes,³ cf. Figure 1b. This is a sensible procedure because of the large difference in naphthol triplet and radical lifetimes. In the least favorable case, i.e., at the lowest benzophenone concentration, first half-lives were 3.2 and 136 μ s, respectively. In addition, to obviate possible problems associated with excited-state concentration changes as a consequence of changing the concentration of the species which absorbs the laser light (benzophenone), the laser energy was suitably attenuated by means of metal-coated filters. Maximum optical densities of naphthol triplet were therefore low and reasonably uniform, 0.028 ± 0.008 , and the analyzing light was restricted to a band between 420 and 470 nm (Balzer K45 interference filter); detection system details have been described.⁴ In Figure 1 is shown the resulting plot of k' vs. benzophenone concentration, each point corresponding to an average of five shots. The arrows indicate the concentration range over which Shizuka

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et al. claim curvature. Clearly such curvature does not exist; neither therefore does the necessity to invoke kinetically significant triplet exciplex intermediacy.

It is also important to point out that aliphatic alcohols are much stronger bases than aromatic ketones.⁵ It is therefore inconceivable that benzophenone ($\sim 10^{-2}$ mol L⁻¹) could compete with methanol (~ 25 mol L⁻¹) as an acceptor of a hydrogen bond from the naphthol triplet. What is to be anticipated, however, is that the H-abstraction process under consideration would be hindered by methanol hydrogen bonding. In agreement with this conclusion, the plot in Figure 1 yields a rate constant for H-abstraction of 2.2×10^7 L mol⁻¹ which is 2 orders of magnitude smaller than the corresponding value for benzene, 3.2×10^9 L mol⁻¹ s⁻¹.^{2,6}

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(6) Strictly linear plots of k' vs. benzophenone concentration have also been obtained for this system in acetonitrile/water (4:1). In this case the naphthol triplet lifetime (6 μ s) was very similar to that in methanol (7 μ s) and the rate constant for H-abstraction somewhat higher (7.2×10^7 L mol⁻¹ s⁻¹).

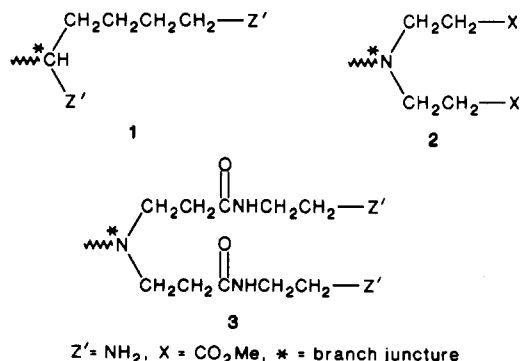
Starburst Dendrimers. 3. The Importance of Branch Junction Symmetry in the Development of Topological Shell Molecules

Donald A. Tomalia,* M. Hall, and David M. Hedstrand

Functional Polymers/Processes Laboratory
Dow Chemical, Midland, Michigan 48640

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A theoretical report by Maciejewski¹ proposed that XRY_n type monomers (where $n = 2$) should lead to hollow, "shell-like" globular molecules if allowed to propagate to a cascade branched structure. The topology and dimensions of these proposed structures were of particular interest to us in that they appeared to be "covalently fixed" mimics of micelles yet they possessed unique hollow interiors usually associated with liposomes (vesicles).^{2a-c} Denkwalter et al.³ synthesized a series of lysine-derived globular structures which fit Maciejewski's criteria; however, they possessed unsymmetrical and unequal branch segments as illustrated by 1.



- (1) Maciejewski, M. J. *Macromol. Sci., Chem.* **1982**, *A17*(4), 689-703.
 (2) (a) Calvin, M. *Acc. Chem. Res.* **1978**, *1*, 369. (b) Kunitake, T.; Okahata, Y.; Shimomura, M.; Yasunumi, S.; Takarabe, K. *J. Am. Chem. Soc.* **1981**, *103*, 5401. (c) Akimoto, A.; Dorn, K.; Gros, L.; Ringsdorf, H.; Schupp, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 90.
 (3) Denkwalter, R. G.; Kolc, J.; Tukaszewski, W. J. U.S. Patent 4 289 872, 1981.

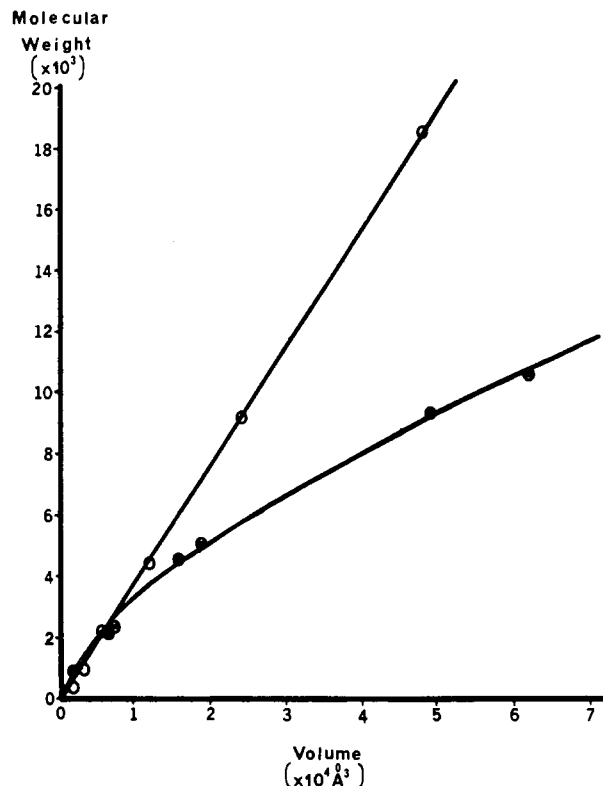


Figure 1. Comparison of the relationship between volume and molecular weight of Denkwalter cascade molecules (O) and starburst dendrimers: (●) ester-terminated dendrimers (2); (⊙) amine-terminated dendrimers (3).

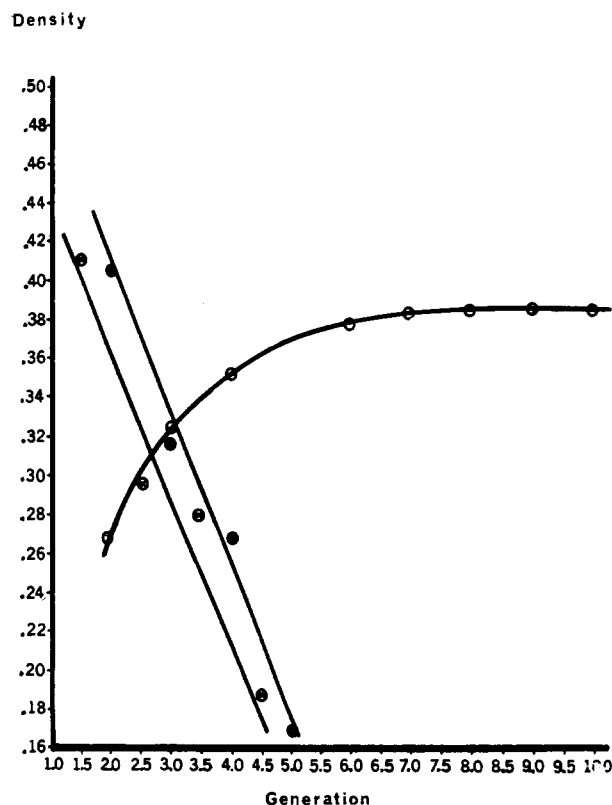


Figure 2. Concentration ($\text{amu}/\text{\AA}^3$) of polymer within solvent-filled microdomains of Denkwalter cascades (O) and starburst dendrimers: (⊙) ester family (2); (●) amine family (3).

Recently, we reported the synthesis^{4a-c} of radially symmetrical three-directional molecules, coined "starburst dendrimers", with