

phosphorus substituents. We expect that this one-pot, three-component, 2 + 2 + 2 reaction sequence will find many different applications for preparation of useful synthetic intermediates and valuable natural products containing various cyclohexenyl or cyclohexenyl-derived structural and functional units.

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Supplementary Material Available: ^1H NMR, IR, mp, and elemental analysis data for products 3-9 (1 page). Ordering information is given on any current masthead page.

Barrier to Coupled Internal Rotation in Di-9-triptycyl Ether. Kinetics of Intramolecular Exciplex Formation in Racemic 2,3-Benzo-9-triptycyl 2-[(Dimethylamino)methyl]-9-triptycyl Ether

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Di-9-triptycylmethanes and di-9-triptycyl ethers (Tp_2X , X = CH_2 and O, respectively) are unique in that two torsional degrees of freedom are very mobile and yet perfectly coupled in the double-rotor molecules. As a stereochemical consequence, new stereoisomerism due to a different phase relationship of the appropriately labeled benzene rings was generated.^{1,2} Since the two wheels of the "bevel gear" were tightly meshed, the gear-slipping process was found to require an activation energy of 32-33 and 42-43 kcal/mol for Tp_2CH_2 and Tp_2O , respectively. One last remaining question as regards the stereochemistry and dynamics of these molecules is how fast the geared rotation is taking place and/or how high the barrier to that torsional motion is. Our preliminary NMR study on these di-9-triptycyl derivatives has shown the presence of only one kind of the averaged benzene ring at temperature as low as -94°C , placing the highest limit of the activation energy value for the coupled rotation at ca. 7-8 kcal/mol.^{1,3} We therefore thought the system would be appropriate for inspection of exciplex fluorescence dynamics⁴ and

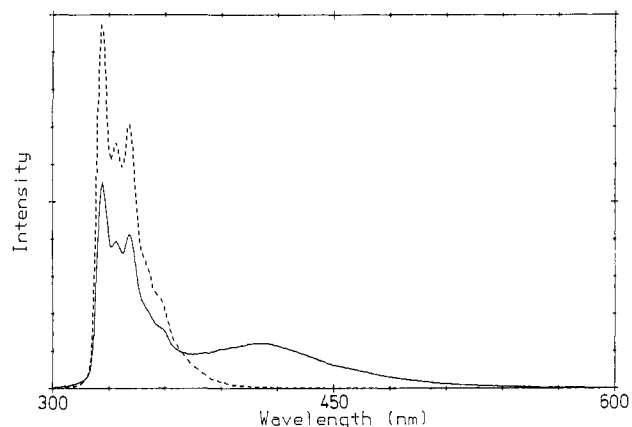
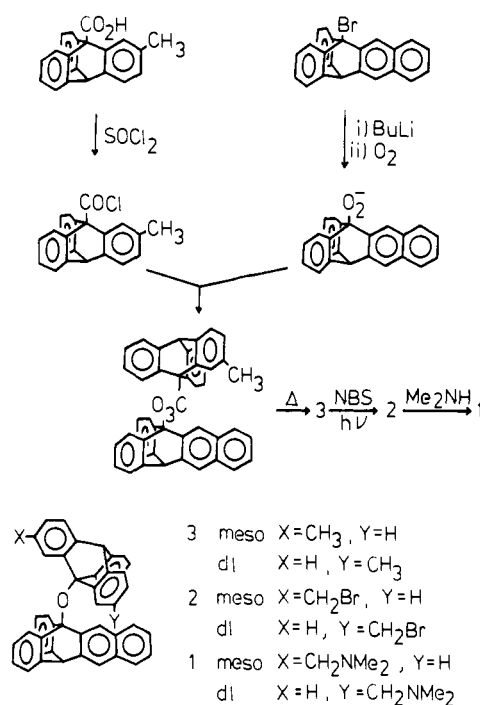


Figure 1. Emission spectra of **1** obtained by excitation at 290 nm in *n*-Bu₂O at 23 °C: (—) racemic isomer; (---) meso isomer.

Scheme I



designed Tp_2O derivative **1**, carrying an aliphatic tertiary amino group on one of the Tp unit and a naphtho chromophore on the other. We wish to report here the preparation and photostationary analysis of the internal exciplex formation of such an "exciplex gear molecule".

Preparation of the geared ether was performed as shown in Scheme I in a manner similar to those previously developed for other Tp_2O compounds.¹ The ether was separated into the racemic and meso isomers by means of HPLC on microsilica with CH_2Cl_2 -MeOH elution. The structural assignment was made straightforward by the comparison of their ^{13}C NMR spectra; the racemic and meso isomers exhibited 15 and 11 lines for the quaternary benzene ring carbons, respectively. The absorption spectra of the two isomers of **1** and an isomeric mixture of **3** were superimposable to one another in various solvents. One can conclude that there is no meaningful interaction between tertiary amino donor (D) and naphthalene acceptor (A) in the ground state.

The fluorescence spectra of the isomers obtained by excitation at the naphthalene chromophore are presented in Figure 1. The racemic isomer of **1** has a broad and structureless emission at longer wavelength (max at 412 nm in *n*-Bu₂O at 23 °C) due to exciplex (D-A*) formation in addition to the emission from locally excited naphthalene (A*). On the other hand, the meso isomer

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- (2) (a) Hounshell, W. D.; Johnson, C. A.; Guenzi, A.; Cozzi, F.; Mislow, K. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6961. (b) Cozzi, F.; Guenzi, A.; Johnson, C. A.; Mislow, K.; Hounshell, W. D.; Blount, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 957. (c) Johnson, C. A.; Guenzi, A.; Mislow, K. *Ibid.* **1981**, *103*, 6240. (d) Johnson, C. A.; Guenzi, A.; Nachbar, R. B., Jr.; Blount, J. F.; Wennerström, O.; Mislow, K. *Ibid.* **1982**, *104*, 5163. (e) Bürgi, H.-B.; Hounshell, W. D.; Nachbar, R. B., Jr.; Mislow, K. *Ibid.* **1983**, *105*, 1427. (f) Guenzi, A.; Johnson, C. A.; Cozzi, F.; Mislow, K. *Ibid.* **1983**, *105*, 1438.
- (3) The barrier heights of 0.19 and 0.93 kcal/mol are predicted by empirical force field calculations for the interconversion of the preferred C₂ conformations of Tp_2CH_2 and the C₂ conformations of Tp_2O , respectively.^{1b,2c}
- (4) (a) Stevens, B. *Adv. Photochem.* **1971**, *8*, 161. (b) Klöpffer, W. In "Organic Molecular Photochemistry"; Birks, J. B., Ed.; Wiley: New York, 1973. (c) Van der Auweraer, M.; Gilbert, A.; De Schryver, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 4007. (d) Mees, F.; Van der Auweraer, M.; De Schryver, F. C. *Ibid.* **1980**, *102*, 4017. (e) Geladé, E.; Boens, N.; De Schryver, F. C. *Ibid.* **1982**, *104*, 6288.

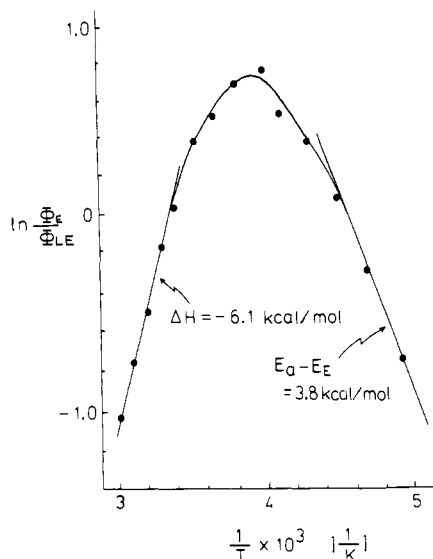


Figure 2. Effect of the temperature on the ratio of the quantum yields of fluorescence from the exciplex and locally excited states of the racemic isomer of **1**.

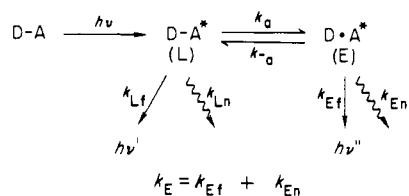
showed only the latter emission. The different emission character of the two isomers is consistent with the structural features of the stereoisomerism.¹ The exciplex fluorescence in the racemic compound indicates that when **A*** is formed by light absorption internal rotation takes place during the lifetime of **A*** to bring **D** to the proximity and generate **D·A*** complex. There is no such conformation accessible in the meso isomer. The processes are formulated as in Scheme II, where k_r and k_n are the radiative and nonradiative decay constants, respectively. In *n*-Bu₂O at 23 °C, the quantum yields of fluorescence of the locally excited naphthalene (Φ_L) and exciplex (Φ_E) were 0.068 and 0.070, respectively. The fluorescence quantum yield of the meso isomer was 0.19. Under photostationary conditions, $\Phi_E/\Phi_L = k_a k_{E_f}/k_{L_f}(k_{-a} + k_E)$. Therefore the temperature dependence of the ratio Φ_E/Φ_L is related to the activation energy ($E_a - E_E$) and enthalpy (ΔH°) of formation of **D·A***.⁴ Such plots are given in Figure 2. In the high-temperature region, $k_E \ll k_{-a}$ and therefore $\ln(\Phi_E/\Phi_L) = -\Delta H/RT$. In the low-temperature region, $k_E \gg k_{-a}$ and therefore $\ln(\Phi_E/\Phi_L) = -(E_a - E_E)/RT$. The E_a and ΔH° values in *n*-Bu₂O were obtained as 4.8 and -6.1 kcal/mol, respectively.⁵

In reference to Scheme II, the E_a value is associated with the height of the barrier over which the conformer with proximal **D** and **A*** is formed from the one with distal **D** and **A*** via torsional motions.⁶ Whereas the naphtho group is in the electronic excited state, the gear framework of the molecule should not be very

(5) The E_E value was found independently by a transient experiment to be 0.98 kcal/mol (to be published).

(6) May we equate E_a to the activation energy to the geared rotation in **1**? The (dimethylamino)methyl group is considered to have additional modes of freedom, torsion around the CH₂-NMe₂ bond and nitrogen inversion, which might be attributed to the observed activation energy. According to DNMR experimental data, the barriers to these motions in appropriately substituted amines are in the range 6–8 kcal/mol: (a) Asahi, Y.; Numata, M.; Mizuta, E. *Chem. Pharm. Bull.* **1973**, *21*, 112. (b) Bushweller, C. H.; Anderson, W. G.; Stevenson, P. E.; Burkey, D. L.; O'Neil, J. W. *J. Am. Chem. Soc.* **1974**, *96*, 3892. (c) Sternhell, S. In "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackson, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; Chapter 6. The observed value is slightly too low to be assigned to such processes. In this connection, the obtained E_a of 4.8 kcal/mol is reasonably assigned to that required for torsion around the ether bond, namely, geared rotation. There may be intrinsic activation energy necessary for the formation of **D·A*** in which the amino group is thought to assume the planar configuration; a certain amount of energy of activation is needed for the configurational change. It is well established that **D·A*** is stabilized by solvation at the cost of a small amount of activation energy.⁴ In other words, the E_a value may contain the barrier due to frictional forces with solvent molecules; See, for example: (a) Velsko, S. P.; Fleming, G. R. *J. Chem. Phys.* **1982**, *76*, 3553. (b) Velsko, S. P.; Fleming, G. R. *Chem. Phys.* **1982**, *65*, 59. If these activation energy values are not negligibly small, the observed value of 4.8 kcal/mol has to be taken as the upper limit of the unimolecular torsional barrier.

Scheme II



different from that of the ground state. Therefore the E_a value of 4.8 kcal/mol is concluded to be a good measure of the barrier height to the gear-meshing process of **1**.⁶

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Registry No. *dl-1*, 94800-91-6; *meso-1*, 94842-45-2.

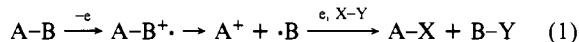
Novel Nucleophilic Substitution Reaction by Radical Cation Intermediates. Photosensitized Transacetalization via S₀N1 Mechanism

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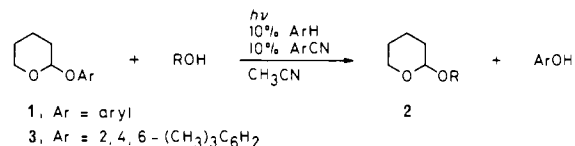
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Generation of radical cations provides a new way to activate organic molecules.¹ In solution, radical cations can dissociate into the solvent-separated cations and radicals, thereby offering opportunities of a new type of metatheses (eq 1).² We disclose



here a newly designed substitution reaction involving a photo-stimulated one-electron-transfer process.³

What appeared to be crucial for the reaction of eq 1 to proceed smoothly were (1) relatively low oxidation potential of substrate **A-B**, (2) high stability of **A*** and **B·**, and (3) a suitable redox system allowing facile back electron transfer to convert **B·** to **B⁻**. We found that transacetalization between aryl 2-tetrahydropyranyl ethers (**1**) and alcohols, giving **2** and phenols, was effected by the



photoexcitation technique using a binary sensitizing system consisting of a light-absorbing, condensed aromatic hydrocarbon and a non-light-absorbing cyano aromatic compound.⁴ Table I lists

(1) A pertinent review on gas-phase reactions: Morton, T. H. *Tetrahedron* **1982**, *38*, 3195-3243.

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(3) Reviews on photostimulated one-electron-transfer reactions: Albini, A. *Synthesis* **1981**, 249-264. Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80-86. Mattes, S. L.; Farid, S. In "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York and Basel, 1983; Vol. 6, pp 233-326.

(4) Pac, C.; Nakasone, A.; Sakurai, H. *J. Am. Chem. Soc.* **1977**, *99*, 5806-5808. Majima, T.; Pac, C.; Nakasone, A.; Sakurai, H. *Ibid.* **1981**, *103*, 4499-4508. Majima, T.; Pac, C.; Sakurai, H. *Ibid.* **1980**, *102*, 5265-5273; *J. Chem. Soc., Perkin Trans. 1* **1980**, 2705-2708; *Chem. Lett.* **1979**, 1133-1136. Gotoh, T.; Kato, M.; Yamamoto, M.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 90-91. Tazuke, S.; Kitamura, K. *Ibid.* **1977**, 515-516. Schaap, A. P.; Lopez, L.; Anderson, S. D.; Gagnon, S. D. *Tetrahedron Lett.* **1982**, *23*, 5493-5496. Schaap, A. P.; Lopez, L.; Gagnon, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 663-664. Schaap, A. P.; Siddiqui, S.; Gagnon, S. D.; Lopez, L. *Ibid.* **1983**, *105*, 5149-5150.