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Intramolecular Photoinduced Electron Transfer: A Dimethylaniline Constrained to the Face of a Naphthalene through a Bicyclic Scaffold

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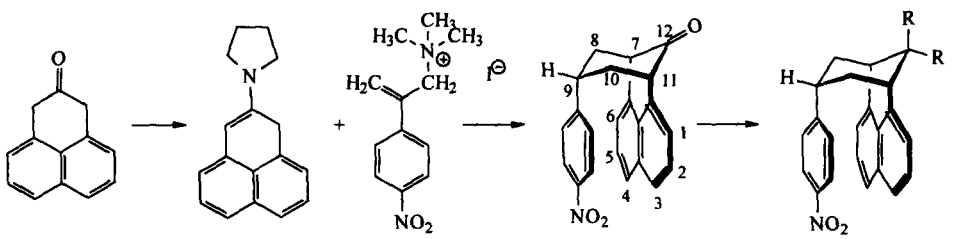
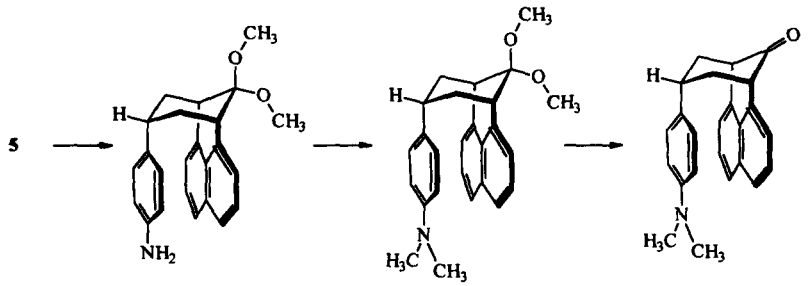
Abstract: The α, α'-annelation of the enamine of 1,3-dihydro-2-phenalenone with ETAC-I [2-(*p*-nitrophenyl)allyl trimethylammonium iodide] affords an aromatic bicyclic framework, 9-*endo*-*p*-nitrophenyl-8,9,10,11-tetrahydro-7,11-methano-12-keto-7H-cyclooocta(*de*)naphthalene having the *p*-nitrophenyl group positioned over the naphthalene ring. The X-ray structure of a derivative was obtained. The nitro function was transformed to a dimethylamino group giving a molecule well suited to evaluate intramolecular photoinduced electron transfer [PET] between the two aromatic elements. The charge transfer [CT] was determined using solvents of different polarity in the examination of the fluorescence spectra. © 1997 Elsevier Science Ltd.

The α, α'-annelation[2,3] of cyclic ketones provides bicyclic structures having unique and discrete stereochemistries. There is an almost effortless creation of structures having the activating function necessary for the sequential Michael reactions positioned in the least stable *endo* configuration. We were curious to test whether this reaction could also be used to fabricate bicyclic structures that would constrain two aromatic rings in a parallel—or almost parallel—face-to-face orientation. We anticipated such structures might be useful for the study of both inductive electronic effects and intramolecular photoinduced electron charge transfer.[4] Indeed, such scaffolds are constructed in good yield and in a single step from the enamine **2** of 1,3-



1 **2** **3** **4** **5**

dihydro-2-phenalenone[5–8] [**1**] and 2-(*p*-nitrophenyl)allyl trimethylammonium iodide [**3**[2f], ETAC-I] in acetonitrile giving 9-*endo*-(*p*-nitrophenyl)-8,9,10,11-tetrahydro-7,11-methano-12-keto-7H-cycloocta(*de*)-naphthalene[9] [**4**]. The relationship of the *p*-nitrophenyl and naphthalene rings was obvious from the complimentary NMR shielding effects[10] on the aromatic rings and an X-ray structure, obtained on the dithioketal derivative [**5**[11], R=$SC_6H_4CH_3$], confirmed this configuration [Figure 1]. The position of the keto function provides access to many different derivatives for the study of electronic transmission effects through or between multiple aromatic rings.



6 7 8

The nitro function was transformed into the dimethylamino group by protection of the carbonyl as a dimethoxyketal[12] **5** [R=OCH_3] with a trace of acid in methanol, sodium borohydride-10% palladium/C reduction[13] of the *p*-nitro function to the amine **6**[14] followed by formaldehyde/cyanoborohydride reduction[15] to the *p*-dimethylaminophenyl ketal **7**.[16] This was hydrolyzed to the dimethylaminophenyl ketone **8**[17] with dilute aqueous HCl.

The system's rigid, fixed and almost parallel [~6° from parallel] orientation of the dimethylaniline moiety with respect to the naphthalene ring [extrapolated from Figure 1] suggested an examination of the fluorescence spectra of these compounds as a function of solvent polarity.[18,19] We believe the structure is unique for these studies because the small distance [~3Å] between the two rings does not allow significant solvent intercalation and the σ bonds of the scaffold are not aligned to allow interaction through the σ system.[20] The dimethylaminophenyl ketal **7** [$1.0x10^{-5}$ M in the indicated solvent, excited in each case at 286 nm] showed, in toluene, an emission band from the locally excited naphthyl group at λ_{MAX} 337 and a charge transfer (CT) band at λ_{MAX} 420. As the solvent polarity was increased, the locally excited naphthyl group emission decreased and there is a distinctive red shift of the CT band [Figure 2, panel 1]. This red shift continued, CH_2Cl_2 [λ_{MAX} 449], EtOH [λ_{MAX} 462], CH_3CN [λ_{MAX} 466], MeOH [λ_{MAX} 474] and even in mixtures of methanol:water [Figure 2, panel 2] with an eventual fluorescent CT red shift to λ_{MAX} 508 nm in 3:7 methanol-water. The corresponding ketone **8** had similar CT bands in CH_2Cl_2 [λ_{MAX} 459] and in CH_3CN [λ_{MAX} 472] but solution in EtOH [λ_{MAX} 464] or in MeOH [λ_{MAX} 470], showed CT bands that only

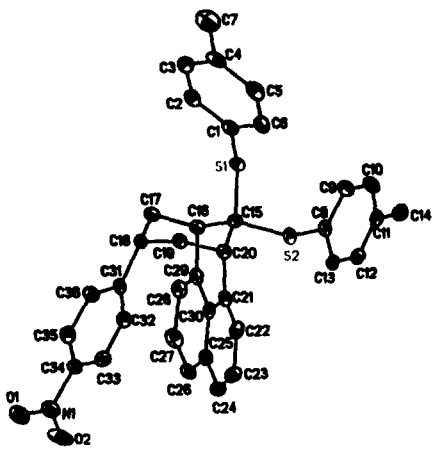


Figure 1

evolved slowly over 24 hours. The blue shift of the CT band of ketone **8** in methanol and ethanol relative to the band in CH_3CN as compared with that of ketal **7** in the same solvents and the slow evolution of these bands, suggest the CT bands in these solvents are due to the equilibrium formation of the respective hemiketals. The system lends itself to many interesting avenues for study.

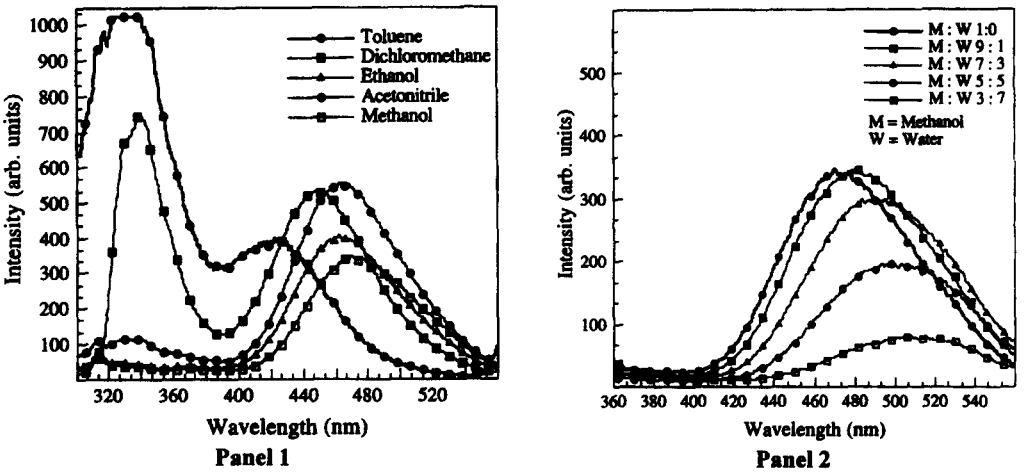


Figure 2. Dimethylaminophenyl ketal **7** [1.0×10^{-5} M] in the indicated solvents. Excitation at 286 nm. Panel 1 fluorescent emmision for toluene through MeOH. Panel 2 fluorescent emmision in mixtures of $MeOH:H_2O$.

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9 4-Nitrophenyl ketone **4**: 69% yield, mp 149-150°C. FT IR (KBr) 3058, 1731, 1594, 1508, 1342, 1111, 836, 777. ^{1}H NMR ($CDCl_3$) δ 7.58 (dd, *J*=7.0, 2.0 Hz, 2H), 7.50 (dd, *J*= 9.0, 1.0 Hz, 2 H), 7.36(t, *J*=7.0 Hz, 2H), 7.24 (dd, *J*=7.0, 1.0 Hz, 2H), 6.86 (dd, *J*=9.0, 1.0 Hz, 2H), 3.94 (dd, *J*=4.9, 3.3 Hz, 2H), 3.26-3.19 (m, 1H), 2.91-2.77 (m, 4H). ^{13}C NMR ($CDCl_3$) δ 211.1, 149.3, 145.1, 137.9, 133.0, 129.0, 126.9, 126.5, 125.8, 124.3, 121.9, 51.7, 40.4, 34.1. Anal. Calcd. For $C_{22}H_{17}NO_3$ C. 76.95; H, 4.99; N, 4.08. Found: C, 76.72; H, 5.07; N, 3.96. The CA numbering of the ring system is placed on formula **4**.

10 The 4-nitrophenyl protons of **4** at positions 2 & 6 reside at δ 6.86, those at positions 3 & 5 reside at δ 7.50 compared with 3-(4-nitrophenyl)bicyclo[3.2.1]octan-8-one [mp 113°C, from cyclopentanone enamine and **3**] having 4-nitrophenyl protons at positions 2 & 6 at δ 7.40 and at positions 3 & 5 at δ 8.17.

11 *bis*(*p*-tolylthio) ketal **5** [R= $SC_6H_4CH_3$]: mp 219°C. FT IR (KBr) 2949, 2919, 1596, 1449, 1392..^{1}H NMR ($CDCl_3$) δ 7.93(d, *J*= 8.1 Hz, 2H), 7.34-7.30(m, 4H), 7.27(d, *J*= 7.7 Hz, 2H), 7.21(t, *J*= 7.7 Hz, 2H) 7.15-7.06(m, 4 H), 6.43(d, *J*= 8.9 Hz, 2H), 3.28-3.24(m, 5 H), 2.53-2.48(m, 2H), 2.45(s, 3H), 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 151.0, 144.0, 139.2, 139.1, 137.2, 137.0, 135.7, 132.2, 131.6, 129.9, 129.0, 128.3, 127.7, 126.8, 125.7, 124.8, 121.2, 70.2, 43.5, 32.3, 31.8, 21.6. HRMS $C_{36}H_{31}NO_4S_2$ $[M+NH_4]^+$: 591.2140, found 591.2125

12 dimethoxy ketal **5** [R= OCH_3]. mp 183-184°C. FT IR (KBr) 2947, 2908, 1515, 1505, 1341, 1103, 1087..^{1}H NMR ($CDCl_3$) δ 7.36-7.20 (m, 8H), 6.54(dd, *J*=9.0, 1.2 Hz, 2H),3.60(t, *J*=2.2 Hz, 2H), 3.44(s, 3H), 3.12-3.08(m, 1H), 3.01(s, 3H) 2.69-2.57(m, 4H). ^{13}C NMR ($CDCl_3$) δ 150.6, 137.7, 132.4, 130.9, 128.3, 126.2, 125.6, 124.9, 124.4, 121.0, 100.3, 45.7, 41.2, 32.6, 31.9. HRMS Calc: $C_{24}H_{23}NO_4$: 389.1627. Found: 389.1627

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14 Amine **6**: mp 160-161°C. FT IR (KBr) 3447, 3362, 1625, 1599..^{1}H NMR ($CDCl_3$) δ 7.38(dd, *J* = 7.3, 2.1 Hz, 2 H), 7.25-7.18(m, 4H), 6.18(dd, *J* = 8.6, 0.8 Hz, 2H), 5.88 (d, *J* = 8.6 Hz, 2H), 3.55(t, *J* = 2.8 Hz, 2H), 3.43(s, 3H), 3.06(t, *J* = 7.0 Hz, 1H), 3.00(s, 3H), 2.61-2.54(m, 2H), 2.49-2.47(m, 2H). ^{13}C NMR ($CDCl_3$) δ 142.0, 138.9, 133.6, 132.6, 131.0, 125.8, 125.6, 125.4, 124.1, 113.6, 101.1, 47.51, 47.48, 41.3, 32.8, 31.2.

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16 Dimethylaminophenyl ketal **7**: mp 112-113°C. FT IR (KBr) 3040, 2949, 1600, 1481, 1454, 1216. ^{1}H NMR ($CDCl_3$) δ 7.34(dd, *J* = 6.5, 3.0 Hz, 2H), 7.24-7.19 (m, 4H), 6.29(dd, *J* = 9.0, 0.9 Hz, 3H), 6.00(d, *J* = 9.0 Hz, 2H), 3.56(t, *J* = 2.8 Hz, 2 H), 3.43(s, 3H), 3.12-3.06(m, 1H), 3.01(s, 3H), 2.64(s, 6H), 2.61-2.54(m, 2H), 2.50-2.44(m, 2H). ^{13}C NMR ($CDCl_3$) δ 147.4, 138.9, 132.6, 132.2, 130.8, 126.0, 125.29, 125.27, 124.9, 124.0, 112.2, 101.1, 47.5, 47.4, 41.3, 41.2, 32.7, 31.1. Calc. for: $C_{26}H_{29}NO_2$ C, 80.59; H 7.54; N, 3.61. found C, 80.12; H, 7.50, N, 3.68.

17 Dimethylaminophenyl ketone **8**: mp 104°C. FT IR (KBr) 2945, 2930, 1736, 1613, 1594, 1442, 1390, 1246. ^{1}H NMR ($CDCl_3$) δ 7.70(dd, *J* = 8.4, 1.0 Hz, 2H), 7.44(dd, *J* = 8.4, 7.0 Hz, 2H), 7.23(dd, *J* = 7.0, 1.0 Hz, 2H), 6.83(d, *J* = 8.7 Hz, 2 H), 3.89-3.85(m, 2H), 2.95-2.78(m, 3H), 2.82(s, 6H), 2.37-2.30(m, 2H). ^{13}C NMR ($CDCl_3$) δ 213.1, 149.1, 140.0, 133.8, 131.0, 127.0, 126.9, 126.7, 126.6, 123.9, 112.5, 50.8, 43.0, 40.7, 34.2. HRMS Calc: $C_{24}H_{23}NO$: 341.1780. Found: 341.1778.

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