Perturbation of the Excited-State Properties of *trans*,*trans*-1,5-Bis(4-(dimethylamino)phenyl)-1,4-pentadien-3-one through Adduct Formation and Silica Gel Adsorption

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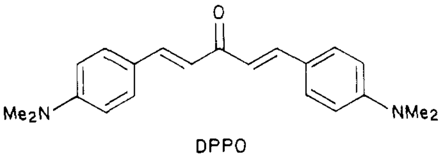
The electronic spectra, luminescent properties, and photoreactivity of the title compound, DPPO, have been investigated in several chemical environments. Solutions which are 0.5 to 100 mM DPPO in CH_2Cl_2 at 295 K emit efficiently with a quantum yield, ϕ_r, of ~0.1–0.2. Over this same concentration range, DPPO also undergoes a [2 + 2] cycloaddition reaction, likely from a different excited state, with a disappearance quantum yield, ϕ_d, which increases from ~0.01 to 0.08. The sensitivity of these excited-state properties to environment is demonstrated by the effects of adduct formation with lanthanon(III) β-diketonate complexes, $Ln(fod)_3$ (Ln = La, Pr, Eu, Yb, Lu; fod is 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate), and adsorption onto silica gel. In the former case, formation of 1:1 DPPO/$Ln(fod)_3$ adducts (formation constant ~10^5 M^{-1}) is evidenced by a ~4000-cm^{-1} red shift in the lowest energy absorption band maximum. The adducts are relatively photoinert ($\phi_d \lesssim 10^{-4}$), and their emission, also substantially red-shifted relative to DPPO (~2400 cm^{-1}), spans several orders of magnitude in efficiency. The adducts' radiative efficiencies are indicative of a paramagnetic quenching mechanism: The paramagnetic Pr, Eu, and Yb derivatives emit more weakly than DPPO (ϕ_r ~10^{-3} to 10^{-2}), whereas the closed-shell La and Lu derivatives approach unit efficiency. Adsorption of DPPO onto silica gel and suspension of the support in cyclohexane to form a slurry also produces a substantial red shift (~3200 cm^{-1}) in λ_{max} of the lowest energy absorption band. Photoreactivity is minimal ($\phi_d \lesssim 10^{-4}$) in this environment, but adsorption causes a ~3700-cm^{-1} red shift in the emission band maximum relative to cyclohexane solution and produces an enhancement in ϕ_r from ~4×10^{-4} to 0.02. Steric and electronic features that may contribute to these substantial environmental effects are discussed.

Introduction

The use of environment as a tool for influencing molecular electronic structure and excited-state properties is under intense investigation. Representative of physicochemical perturbations are those introduced by micelles, intercalation, adduct formation, and adsorption. We have found particularly dramatic effects by exploiting adduct formation and adsorption onto silica gel using retinal isomers and (arene)tricarbonylchromium(0) complexes as probe molecules: With retinal, complexation with the Lewis acid tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium(III), $Eu(fod)_3$,[1] or adsorption onto silica gel[2] leads to novel photoisomerization paths; for the Cr(0) complexes, such experiments[3,4] alter the efficiency for photodissociation of the CO ligand.

While conducting these studies, we became aware of diarylidene ketones as another class of compounds having excited-state properties with the potential for susceptibility to environmental control. Derivatives of *trans,trans*-1,5-diphenyl-1,4-pentadien-3-one (dibenzylideneacetone), for example, exhibit electronic spectra that are strongly solvent dependent.[5] In addition, dibenzylideneacetone is known to undergo a photoinduced [2 + 2] cycloaddition reaction with itself,[6] and several of its dimethylamino derivatives emit at 295 K in fluid solution.[7]

These results prompted us to investigate the excited-state properties of the title compound, DPPO. We report



DPPO

in this paper that DPPO exhibits an efficient [2 + 2] cycloaddition photoreaction as well as efficient emission at 295 K in CH_2Cl_2 solution. Moreover, both of these processes are greatly affected by adduct formation with $Ln(fod)_3$ complexes (Ln = La, Pr, Eu, Yb, Lu) and by adsorption onto silica gel.

Results and Discussion

Sections below describe the excited-state properties of DPPO in CH_2Cl_2 solution, of its adducts with $Ln(fod)_3$ complexes in CH_2Cl_2; and of cyclohexane slurries of DPPO adsorbed onto silica gel. The effects of each of these environments are, in turn, analyzed through electronic spectra, luminescence, and photoreactivity.

A. Solution Studies. 1. Electronic Spectra. Solutions of DPPO in CH_2Cl_2 are orange-yellow. Figure 1 reveals that the color derives from an intense (ϵ ~ 4.1×10^4 M^{-1} cm^{-1}) band with λ_{max} ~440 nm. A $^1\pi,\pi^*$ assignment for the band is reasonable in view of its intensity and red shift with increasing solvent polarity; these properties and spectral characteristics of DPPO derivatives have prompted a description of the transition as an intramolecular charge transfer wherein electron density is shifted from the phenyl to the carbonyl group.[5c,d]

Evidence for aggregation was sought from electronic spectra. Within experimental error, Beer's law was satisfied at 520 nm over a concentration range of 0.5 to 100 mM, indicating that ground-state association is not significant in this system over this concentration regime.

2. Luminescence. In common with a number of compounds containing conjugated dimethylamino and carbonyl groups, DPPO emits at 295 K.[7] The solid emits orange

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(1) Ellis, A. B.; Schreiner, R.; Ulkus, R. A. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 3993–7.

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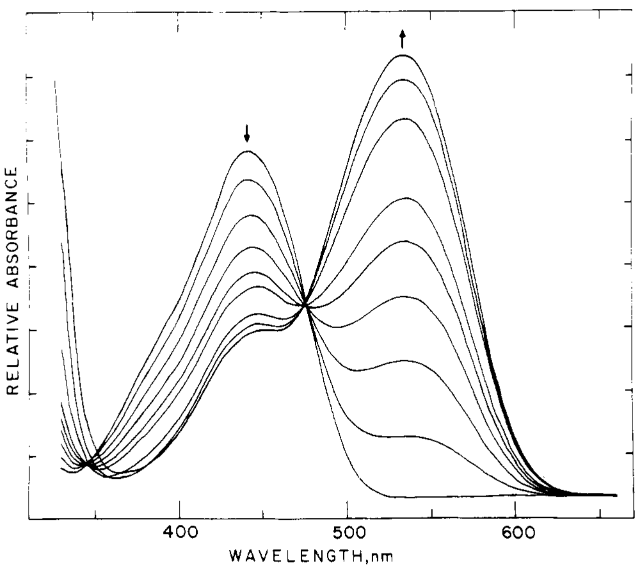

Figure 1. Electronic spectral changes accompanying the addition of a 4.2 mM Eu(fod)$_3$-CH_2Cl_2 solution to a 1.5 × 10^{-5} M DPPO CH_2Cl_2 solution in a 1.0-cm pathlength cell. Curves correspond to addition of 0, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, and 8.0 equiv of Eu(fod)$_3$.

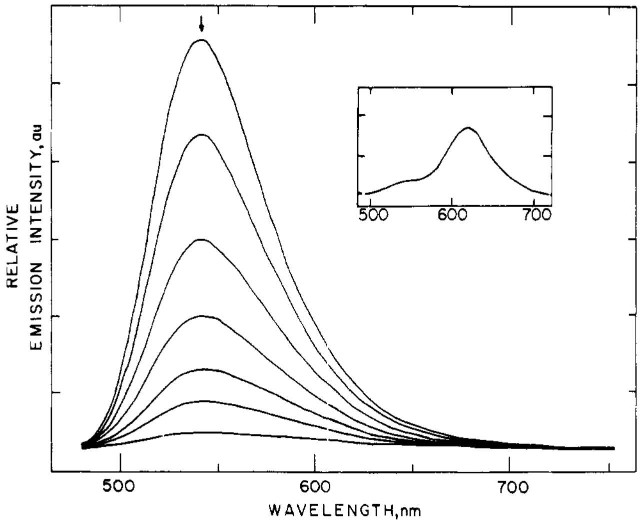

Figure 2. Uncorrected emission spectral changes accompanying the titration of DPPO with Eu(fod)$_3$. Spectra are shown for each solution described in Figure 1 up to 2.0 equiv, using excitation at 475 nm, an isosbestic point. The inset illustrates the spectrum at greater sensitivity when 8 equiv. of Eu(fod)$_3$ have been added.

light with λ_{max} ~590 nm. When dissolved in CH_2Cl_2, however, a dramatic change in the emitted color to bright yellow-green occurs. Figure 2 presents the solution emission spectrum of DPPO, showing it to consist of a broad band with λ_{max} ~540 nm. We are uncertain as to the origin of this band, although its proximity to the 440-nm absorption band and the fast decay time of the emission ($\lesssim$10 ns; limited by N_2 laser pulse duration) are consistent with a transition from a $^1\pi,\pi^*$ excited state. An excitation spectrum of the band mimics the DPPO absorption spectrum.

Radiative quantum yields, ϕ_r, for DPPO in various environments are collected in Table I. An early measurement, in toluene solution, gave a ϕ_r value of ~0.05.[7] We found that CH_2Cl_2 provided a very emissive milieu for DPPO, yielding, in N_2 or air, a solution with $\phi_r \sim 0.2$. This value was roughly constant over a concentration range of 0.5 to 10 mM; at 100 mM, a value closer to 0.1 was measured. The solid is characterized by an efficiency of ~0.1, which does not noticeably increase upon cooling to 77 K.

Table I. Radiative Quantum Yields of DPPO in Various Environments

medium	ϕ_r[a]
solid	0.080[d]
CH_2Cl_2 solution (0.5, 1.0, 10 mM)	0.16
toluene solution[7]	0.051
cyclohexane solution	0.00043
adducts[b]	
La(fod)$_3$	0.69
Pr(fod)$_3$	0.0030
Eu(fod)$_3$	0.0027
Yb(fod)$_3$	0.021
Lu(fod)$_3$	0.76
slurries[c]	
10^{-5} mol DPPO/g silica gel	0.040
10^{-4} mol DPPO/g silica gel	0.015

[a] Radiative quantum efficiency (295 K) obtained with 365-nm excitation as described in the Experimental Section. [b] Values of ϕ_r for ~1 mM CH_2Cl_2 solutions of DPPO containing enough Ln(fod)$_3$ (~8–12 equiv) for full complexation. For the Eu, Yb, and Lu derivatives, emission is assigned to a 1:1 adduct with λ_{max} ~620 nm. For Pr, this adduct is observed as is another with λ_{max} ~670 nm involving presumably a Pr(fod)$_3$ dimer (see text); both emission bands were used in the ϕ_r determination. For La, only the presumed La(fod)$_3$-dimer-based adduct with λ_{max} ~670 nm was observed under the experimental conditions employed. [c] Slurries of DPPO on silica gel at the indicated concentrations, suspended in cyclohexane. [d] This value of ϕ_r was acquired with 436-nm excitation.

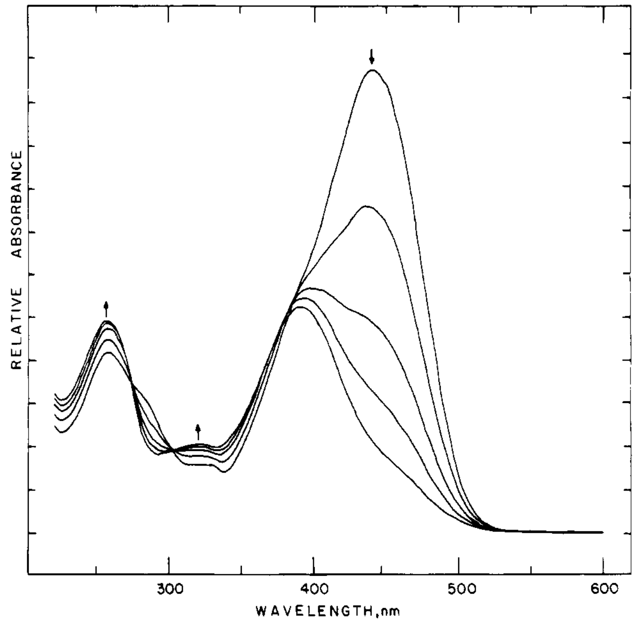

Figure 3. Electronic spectral changes accompanying the 457.9-nm photolysis of a 0.49 mM DPPO CH_2Cl_2 solution in a 0.10-cm path-length cell. The curves shown correspond to 0, 20, 40, 60, and 80 s of photolysis. The entire solution (~1.5-cm^2 cell window area) was irradiated with ~16 mW of power.

3. Photochemistry. We anticipated photoreactivity from DPPO based on the photoinduced [2 + 2] cycloaddition reaction of dibenzylideneacetone.[6] An intriguing observation for this system was that photolysis in the presence of the Lewis acids UO_2^{2+} or $SnCl_4$ yielded a dimer of different stereochemistry.[8] Related effects have recently been reported by Lewis et al. for the photodimerization of coumarin.[9]

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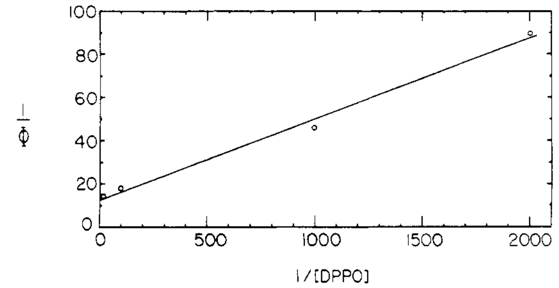
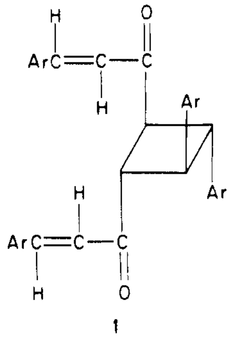


Figure 4. Plot of reciprocal quantum yield for disappearance of DPPO vs. reciprocal molar DPPO concentration in CH_2Cl_2. Data were obtained by use of ~20 mW of 457.9-nm excitation.

Visible photolysis of DPPO causes the orange-yellow solution to become pale yellow. The spectral changes accompanying the reaction are shown in Figure 3; a smooth conversion is evidenced by the isosbestic points at ~385, 304, and 274 nm. After an exhaustive irradiation, subjection of the photolysate to preparative TLC showed it to consist principally of one species. Both mass and ^1H NMR spectroscopy are consistent with formulation of the photoproduct as a cyclobutane derivative. Moreover, the ^1H NMR coupling constants and chemical shifts for the cyclobutane ring protons are very similar to those of the product resulting from photolysis of the unsubstituted parent dibenzylideneacetone.[6] Although we cannot rigorously exclude several other isomers, we presume, based upon the similarity of our spectral data to that reported for the dibenzylideneacetone dimerization product, that our product is 1, formed by head-to-head cycloaddition.



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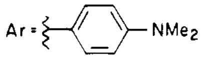

As shown for 1, the ^1H NMR data also indicate a trans geometry about the double bonds.

We have measured the quantum yield for disappearance of DPPO, ϕ_d, as a function of concentration using 457.9-nm excitation. The value of ϕ_d increases with concentration, as expected, from ~0.01 at 0.5 mM to ~0.08 at 100 mM. This variation contrasts sharply with the insensitivity of ϕ_r to concentration, suggesting that emission and photodimerization originate from different excited states. A plot of ϕ_d^{-1} vs. $[DPPO]^{-1}$, presented in Figure 4, is linear, consistent with a mechanistic scheme involving reaction of an excited molecule with a ground-state molecule.[10] Moreover, the intercept-to-slope ratio of ~4×10^2 M^{-1} provides a lower limit of ~40 ns for the excited state's lifetime, assuming a diffusion-controlled bimolecular quenching rate constant of ~10^{10} M^{-1} s^{-1}. Since we did not observe emissive decay on this time scale, this, too, supports the notion that emission and photoreactivity originate from different excited states.

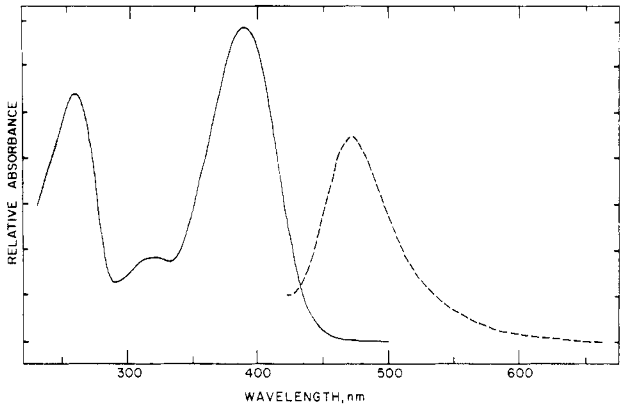

Figure 5. Absorption (solid curve) and uncorrected emission (dashed curve) spectra of a 4.7×10^{-5} M CH_2Cl_2 solution of the product of DPPO photolysis, presumed to be 1. The emission spectrum was obtained with 390-nm excitation.

Mechanistically, the cycloaddition reaction appears to proceed primarily through a singlet excited state. In a triplet sensitization experiment, prolonged photolysis in CH_2Cl_2 of DPPO and Michler's ketone, with almost exclusive excitation of the latter at 334–364 nm, we were unable to observe formation of the unsensitized photoproduct, presumed to be 1; rather, a small quantity of intractable material slowly formed.

An intriguing feature of DPPO's photoreactivity is the apparent absence of geometric isomerization. Given the efficient photoisomerization exhibited by many simple enones,[11] the absence of this process is surprising. Although we cannot exclude its occurrence completely, a mass balance conducted after prolonged direct irradiation (60% conversion of DPPO; 100 mM solution) indicates that the cycloaddition product accounts for at least 93% of the converted DPPO; the balance of the material appeared to be intractable by TLC. We were also unable to see evidence for cis isomers in ^1H NMR spectra of the photolysate mixture, obtained at various intervals during the photolysis. Of course, it is possible that DPPO isomers with a cis geometry are simply unstable with respect to the trans,trans isomer under our experimental conditions.

It is noteworthy, too, that the cycloaddition product of direct DPPO irradiation emits. Figure 5 presents absorption and emission spectra of the species assigned as 1 in CH_2Cl_2 solution. The emission band maximum occurs at 470 nm; a ϕ_r value of ~0.003 was measured in CH_2Cl_2 solution.

B. Adduct Studies. 1. Electronic Spectra. Addition of $Ln(fod)_3$ complexes to solutions of DPPO in CH_2Cl_2 causes a color change to deep red. Figure 1 displays representative spectral changes accompanying a titration of DPPO with $Eu(fod)_3$. The changes are consistent with the formation of a 1:1 DPPO/$Eu(fod)_3$ adduct with a formation constant of ~4×10^5 M^{-1}. With a large stoichiometric excess of $Eu(fod)_3$ present, a limiting spectrum is reached wherein the lowest energy band has red-shifted to ~535 nm and increased in absorptivity relative to DPPO by ~30%. Similar formation constants and band shifts characterize adducts prepared from the other $Ln(fod)_3$ complexes; a modest dependence of the band maximum on lanthanon size was observed with λ_{max} increasing from ~530 nm for $Lu(fod)_3$ to ~540 nm for $La(fod)_3$. These enormous spectral shifts relative to DPPO, ~4000 cm^{-1}, far exceed solvent-induced shifts; for example, λ_{max} for

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DPPO occurs at 400 nm in isooctane, 440 nm in CH_2Cl_2, and 457 nm in EtOH. Only with another Lewis acid, $FeCl_3$, has such a substantial shift—to 667 nm—been observed.[5a]

We attribute the spectral changes observed with mixtures of DPPO and $Ln(fod)_3$ complexes to adduct formation wherein the carbonyl oxygen atom coordinates to the lanthanon ion. This mode of bonding is consistent with both the red shift in the electronic spectrum and the $^1\pi,\pi^*$ assignment for the lowest energy absorption band: The presence of a $Ln(fod)_3$ complex would be expected, through inductive effects, to remove electron density from the carbonyl group. Also supporting this site of interaction are ^1H NMR spectral changes: When a substoichiometric quantity of $Eu(fod)_3$ is added to a $CDCl_3$ solution of DPPO, the magnitude of the displacement in chemical shifts increases with proximity to the carbonyl group; the signals for olefinic protons shift downfield, while the methyl proton resonances are unaffected.

In addition to 1:1 DPPO/$Ln(fod)_3$ adduct formation, the β-diketonate complexes with the two largest lanthanon ions, La and Pr, afforded evidence for a second adduct: Large stoichiometric excesses of these complexes yielded new absorption bands at ~620 nm which we attribute to a complex of DPPO with dimers of $La(fod)_3$ and $Pr(fod)_3$. Evidence for the formation of dimeric species with the larger $Ln(fod)_3$ complexes has been reported from ^1H NMR and vapor-phase osmometric studies.[12]

2. Luminescence. Paralleling their effect on the DPPO absorption spectrum, $Ln(fod)_3$ complexes also profoundly influence the compound's emissive properties. Figure 2 illustrates spectral changes accompanying a titration of DPPO with $Eu(fod)_3$. As the titration proceeds, the intense emission of DPPO is quenched and a weak adduct emission band is observed at ~620 nm, shown in the inset of Figure 2. The adduct-derived band has its maximum red-shifted by ~2400 cm^{-1} from that of uncomplexed DPPO. A similar shift obtains with the other $Ln(fod)_3$ complexes. In titrations with $La(fod)_3$ and $Pr(fod)_3$, large stoichiometric excesses yield a second emission band at ~670 nm, presumably arising from the adduct consisting of DPPO and the dimeric β-diketonate complex whose existence was inferred from analogous absorption spectral changes (vide supra).

For all of the adducts investigated, addition of the $Ln(fod)_3$ complex to solutions of DPPO causes absorption and emission spectra of the solution to change roughly in parallel. A quantitative comparison was made with the DPPO/$Eu(fod)_3$ system: An emission titration, conducted with excitation at the 475-nm isosbestic point, yields a similar formation constant to the spectrophotometrically derived value, indicating that the emission titration is measuring the ground-state rather than excited-state equilibrium. This, in turn, suggests that decay of excited DPPO and of the excited adduct to their respective ground states competes favorably with their interconversion. Experimental support for this scenario comes from the fast decay times ($\lesssim$10 ns) observed for the 540- and 620-nm bands and from the inability to see DPPO emission from exclusive excitation of the adduct at 550 nm when both species are present in solution.

Particularly intriguing are the radiative efficiencies of the adducts, collected in Table I. The dramatic 60-fold reduction in ϕ_r illustrated for the $Eu(fod)_3$ adduct in Figure 2 does not appear to be due to energy transfer to the Eu(III) center: Emission bands characteristic of the lanthanon ion are not observed upon excitation of the adduct. Rather, the Table I data support a paramagnetic quenching mechanism, since $Pr(fod)_3$ and $Yb(fod)_3$, like $Eu(fod)_3$, produce adducts which emit much more weakly than DPPO, with ϕ_r ~10^{-3} to 10^{-2}. In contrast, the diamagnetic Lewis acids $La(fod)_3$ and $Lu(fod)_3$ yield adducts whose emissive efficiencies are nearly unity.

3. Photochemistry. In view of the sensitivity of the stereochemistry of coumarin[9] and dibenzylideneacetone[6,8] photoproducts to Lewis acids, our studies of adduct-mediated photochemistry were surprising. For example, in experiments with partial (~20%) and complete complexation of DPPO (0.5 mM) by $Eu(fod)_3$, exclusive excitation of the adduct at 580 nm yielded only minor spectral changes after prolonged photolysis. Thin-layer chromatography afforded almost complete recovery of DPPO, corresponding to an upper limit on ϕ_d of ~10^{-4}. A similar lack of reactivity was found with 514.5-nm excitation when DPPO is completely bound to any of the $Ln(fod)_3$ complexes.

The loss of reactivity with adduct formation could conceivably arise from both steric and electronic effects. In the former case, the bulky $Ln(fod)_3$ complexes may prevent two DPPO molecules from achieving the proximity necessary for dimerization. Electronically, the red shift in the $^1\pi,\pi^*$ band could correspond to a reordering of excited states which would shut off the photoreaction; such "state switching" has previously been invoked in studies of retinal[2,13] and (arene)$Cr(CO)_3$ complexes[3,4] to account for changes in photoreactivity. Related to these explanations is the possibility that adduct formation is effectively shortening the lifetime of the reactive excited state (we thank a reviewer for this suggestion). To favor reactivity under these conditions, we increased the adduct concentrations in CH_2Cl_2 by using 50 mM DPPO and 400 mM $Ln(fod)_3$ (Ln = Lu or Eu). With neither the diamagnetic nor paramagnetic lanthanon, however, did we see an enhancement in adduct photoreactivity using 514.5-nm excitation, suggesting that this may not simply be a lifetime effect.

C. Silica Gel Studies. Slurries of DPPO, prepared by adsorbing the compound onto nondehydrated silica gel and suspending the support in cyclohexane, were utilized for optical studies. Light scattering in this heterogeneous system is minimized by the match in refractive indices of the solvent and support.[14] The large-pore silica gel employed is characterized by its supplier as having a surface area of ~300 m^2/g, a surface density of ~5 SiOH groups/nm^2, and a pore volume of 1.6 mL/g (average pore radius of ~100 Å).

1. Electronic Spectra. Exposure of yellow cyclohexane solutions of DPPO to nondehydrated silica gel produces slurries that appear blood-red to the eye. Corresponding electronic spectral changes, pictured in Figure 6, indicate an ~3200-cm^{-1} red shift in λ_{max} for the most intense visible transition. At the concentrations employed (~10^{-6} to 10^{-4} mol of DPPO/g of silica gel), essentially all of the DPPO is adsorbed, as evidenced by the absence of DPPO absorption bands in the electronic spectrum of the supernatant liquid.

The DPPO/silica gel interaction appears to be weakly chemisorptive based on the ready desorption of the com-

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[14] Nicholls, C. H.; Leermakers, P. A. *Adv. Photochem.* **1971**, *8*, 315–36 and references therein.

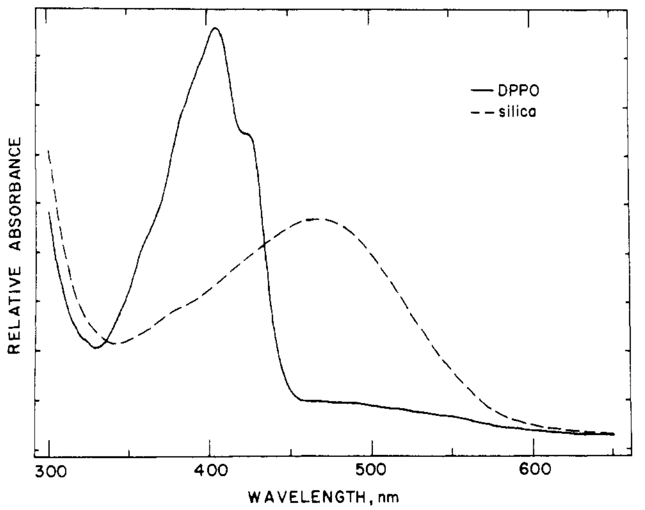

Figure 6. Electronic spectra of DPPO in cyclohexane solution (solid curve) and adsorbed onto silica gel to form a slurry with cyclohexane (dashed curve). The quantity of DPPO adsorbed (~10^{-6} mol of DPPO/g of silica gel) was adjusted to give the same number of molecules in the optical path as were present for the ~0.3 mM solution, shown as the solid curve. A 0.10-cm pathlength cell was employed for both spectra.

pound with CH_2Cl_2. In an effort to identify bonding sites, we attempted to adsorb DPPO onto silica gels which had been dehydroxylated with $(CH_3)_2SiCl_2$ and dehydrated (110 °C at 10^{-5} torr for ≳3 h). We found that adsorption did not occur on the dehydroxylated support but did occur on the dehydrated silica gel. These observations suggest that the silanol groups serve as the primary binding sites.

As for the forces operating in the silica gel/DPPO system, adsorption has generally been described in terms of hydrogen bonding, electrostatic interactions, and dispersion forces.[15] All of these interactions could be significant in this system: In addition to the strong spectral sensitivity to solvent (vide supra), protonation of DPPO in cyclohexane solution with HCl vapor produces a substantial blue shift in λ_{max} to ~310 nm. It should be kept in mind, too, that the spectrum in Figure 6 is an average of contributions from the multiplicity of environments afforded by the support.

A few additional comments on the cyclohexane DPPO system are merited. The hydrocarbon spectrum of Figure 6 exhibits both a low-energy band and structure in the major band which are not seen in the CH_2Cl_2 spectrum of Figure 1. A -60 °C methylcyclohexane spectrum further exaggerates these features: The solution is reversibly thermochromic, acquiring an orange tint at -60 °C, and a vibronic progression with ~1400 cm^{-1} spacings, presumably corresponding to a C=C stretching mode, is evident. We are unable to definitively assign the low-energy peak, although its absorptivity of ≳10^3 M^{-1} cm^{-1} (poor solubility precluded an accurate determination of ϵ) supports a $^1\pi,\pi^*$ assignment.

2. Luminescence. Emissive properties of DPPO are greatly perturbed by adsorption. Visually, barely perceptible yellow-green emission in cyclohexane solution (ϕ_r ~4×10^{-4}) becomes an intense deep red color after adsorption onto silica gel. Figure 7 depicts this effect; the spectral shift in λ_{max} is ~3700 cm^{-1}. Interestingly, the solution emission band roughly matches the low-energy absorption band (Figure 6) in energy. Whether this is an unusually small Stokes shift or emission from an upper excited state is not clear.

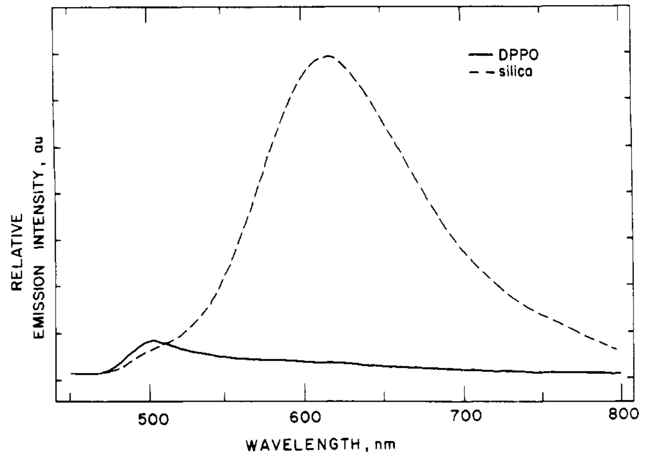

Figure 7. Uncorrected emission spectra of the solution (solid curve) and slurry (dashed curve) samples of Figure 6. Both spectra were recorded at the same sensitivity using 435-nm excitation.

In characterizing the adsorbate's emission, we found that both the spectral distribution and radiative quantum yield (Table I) were slightly dependent on loading over the range of ~10^{-5} to 10^{-4} mol of DPPO/g of silica gel. In the former case, the modest changes observed likely reflect different site occupancies. The trend in ϕ_r is indicative of concentration quenching. Lifetimes measured for these samples were again too fast (≲10 ns) to measure with the N_2 laser/dye laser system employed.

3. Photochemistry. As was the case with adduct formation, adsorption drastically reduces the photoreactivity of DPPO: Prolonged 514.5-nm photolysis of a slurry, followed by desorption with CH_2Cl_2 and TLC analysis, yields virtually quantitative recovery of DPPO; the upper limit on ϕ_d is ~10^{-4}. Loss of reactivity is perhaps not surprising, since molecular proximity and mobility are minimized on the support. As mentioned in connection with adduct formation, there may also be an electronic component to the cessation of reactivity through excited-state reordering.

Summary

The title compound, DPPO, exhibits a rich variation in excited-state properties when placed in different environments. Dramatic shifts in absorption and emission spectra and substantial variations in ϕ_r and in photoreactivity are readily produced by adduct formation and silica gel adsorption. The combinations of steric and electronic factors from which these effects derive clearly provide considerable tunability of molecular excited-state properties.

Experimental Section

Materials. Samples of *trans,trans*-1,5-bis(4-(dimethylamino)phenyl)-1,4-pentadien-3-one (DPPO) were prepared from acetone and *p*-(dimethylamino)benzaldehyde (Aldrich; used as received) by the method of Olomucki and LeGall;[16] the precipitate was recrystallized in toluene (mp 191-2 °C; ^1H NMR ($CDCl_3$) δ 3.03 (s, 12 H), 6.70 (d, 4 H, J = 8.8 Hz), 6.90 (d, 2 H, J = 15.7 Hz), 7.53 (d, 4 H, J = 8.8 Hz), 7.70 (d, 2 H, J = 15.7 Hz). Quinine sulfate dihydrate, $CDCl_3$, and spectrograde cyclohexane and methylcyclohexane were obtained from Aldrich and used as received. Methylene chloride (Fisher) was purified by washing sequentially with concentrated H_2SO_4, 3 N NaOH, and distilled H_2O; the solvent was then distilled from CaH_2 and stored in a

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N_2-filled glove bag. Samples of Eu(fod)$_3$, Yb(fod)$_3$, and Pr(fod)$_3$ were obtained from Aldrich and dried in vacuo over P_2O_5 before use. Samples of La(fod)$_3$ and Lu(fod)$_3$ were synthesized by the method of Sievers and Eisentraut[17] using chloride (Alfa) rather than nitrate salts; Hfod was obtained from Aldrich. Michler's ketone was acquired from Eastman. Large-pore silica gel (Alfa; 70 μm) and dimethyldichlorosilane (Petrarch) were used as received.

Spectra. All solutions were prepared from N_2-purged solvents in a N_2-filled glove bag. Electronic spectra were recorded on a Cary 17D UV–vis–near-IR spectrophotometer. Spectra at −60 °C were obtained using a quartz Dewar with Suprasil windows which mated to the Cary's sample compartment. The sample, contained in a quartz cuvette equipped with a quartz stem for positioning ease, was placed in a brass cell holder which sat on copper coils immersed in an isooctane bath. Nitrogen cooled by passage through copper coils set in liquid N_2 and N_2 at room temperature were mixed and pumped through the isooctane-immersed coils to provide the desired temperature for the isooctane bath. Thermostatic control was provided by an Omega Model 4202 PC2 temperature regulator used in conjunction with an Omega PR 11 resistive temperature device used to probe the bath temperature. Titration techniques in adduct-forming experiments and a BASIC computer program to extract formation constants from these data have been described.[3] Acquisition of slurry spectra has been described including experiments with dehydrated and dehydroxylated supports.[2,4] Uncorrected emission spectra were obtained with an Aminco-Bowman spectrophotofluorimeter equipped with a Hamamatsu R446S PMT; spectra were corrected for detector response as described previously.[18] Emission titrations with Eu(fod)$_3$ were conducted on the same samples used for absorption titrations, and formation constants were extracted with the BASIC program used for the spectrophotometric titrations. In both titrations with Eu(fod)$_3$, the best fit was found by assuming a 1:1 DPPO/Eu(fod)$_3$ adduct stoichiometry. An IBM WP-200 spectrometer provided ^{1}H NMR spectra with Me_4Si serving as an internal standard; coupling constants were calculated from spectra taken on a Bruker WH-270 spectrometer. Mass spectral data for 1 were obtained on a Nicolet FT-MS-1000 instrument (self-chemical ionization).

Photolyses. All photolyses were performed under N_2. Irradiation at 457.9, 514.5, and 334–364 nm (4 laser lines) was conducted with a Coherent Radiation CR-12 Ar^+ laser; excitation at 580 nm employed the Ar^+ laser as a pumping source for a CR 590-03 dye laser. Photolyses were carried out by passing the 2–3-mm diameter laser beam sequentially through a 10X beam expander, Oriel interference filters (fwhm 10 nm) to eliminate plasma background (not used for 334–364-nm excitation), and a mask to just fill the sample with light. Laser power was measured with a Scientech 362 power meter (flat response 250–35000 nm). Photolyses of the silica gel cyclohexane slurries were conducted as previously described,[2] using 2.0 mL of cyclohexane with both 2 mg and 10 mg of DPPO adsorbed onto 0.2 g of silica gel; excitation at 514.5-nm was employed. Photolysates resulting from long-term irradiation of DPPO and adduct solutions were analyzed by preparative TLC using CH_2Cl_2 as the mobile phase; for slurry photolyses, desorption with CH_2Cl_2 preceded TLC analysis. In DPPO photolysis, the isolated product, presumed to be the cyclobutane derivative 1, was characterized by mass spectrometry and ^{1}H NMR: MS, *m/e* 640; ^{1}H NMR (acetone-d_6) δ 2.88 (s, 12 H), 2.99 (s, 12 H), 3.56 and 3.93 (AA′BB′; 4 H), 6.55 (d, 2 H, $J = 16.5$ Hz), 6.67 (d, 4 H, $J = 9.0$ Hz), 6.73 (d, 4 H, $J = 9.0$ Hz), 7.21 (d, 4 H, $J = 9.0$ Hz), 7.29 (d, 4 H, $J = 9.0$ Hz), and 7.35 (d, 2 H, $J = 16.5$ Hz). Coupling constants ($J_{AA'} = 9.3$ Hz; $J_{AB'} = -0.1$ Hz; $J_{AB} = 9.3$ Hz; $J_{BB'} = 9.3$ Hz) were obtained with an iterative computer program;[19] the ^{1}H NMR shifts and coupling constants are similar to those reported for the product of dibenzylideneacetone photolysis.[6] Quantum yields for the disappearance of DPPO, ϕ_d, were determined for initial concentrations of 0.5, 1.0, 10, and 100 mM by monitoring the decline of the DPPO absorption band at 440, 485, 515, and 535 nm, respectively, with total conversion of $\lesssim$25%. Good linearity in the data was found, including extrapolation to zero conversion at zero time. Values of ϕ_d are based on three complete sets of data with five data points per set. The quantum yields are uncorrected for reflective and scattering losses; reproducibility was ±15%. A triplet-sensitized photolysis was conducted with a CH_2Cl_2 solution which was 0.5 mM in DPPO and 3.9 mM in Michler's ketone; the solution was irradiated at 334–364 nm. Adduct photolyses were conducted with 8–10 equiv of the Ln(fod)$_3$ complex and 0.5 and 50 mM DPPO (Ln = Eu, Lu for the 50 mM experiment). Excitation at 514.5 nm was employed; for the Eu(fod)$_3$/DPPO (0.5 mM) experiment, 457.9- and 580-nm light was also used.

Lifetimes and Radiative Quantum Yields. Attempts to acquire lifetimes were made on solid DPPO, on 1 mM CH_2Cl_2 solutions of DPPO and its Eu(fod)$_3$ adduct (8 equiv), and on silica gel slurries of DPPO. Excitation at ~450 nm from a N_2-pumped dye laser was employed, using instrumentation previously described.[20] The emissive quantum yield, ϕ_r, of solid DPPO was obtained as previously described.[20] Solution and slurry quantum yields were determined on the Aminco-Bowman spectrometer with reference to a 5 mM quinine sulfate solution (1.0 N H_2SO_4) for which a ϕ_r value of 0.55 was used;[21] excitation at 365 nm was employed. Measurements were corrected for detector sensitivity as previously described.[18]

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