

# Structural and Spectroscopic Studies of the Photophysical Properties of Benzophenone Derivatives

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## **Supporting Information**

### **Solution Phase Optimizations**

In order to compare gas and solution phase structures of the explicit solvent complexes, optimizations for the DOB:MeOH complex were performed in the presence and absence of a solvent model. The B3PW91/Midi! optimization was performed for DOB with an explicit MeOH molecules in the gas phase, as reported in the text, and using the IEF-PCM solvation model for MeOH in Gaussian 03. The vibrational frequencies of the molecules were calculated to verify the nature of the stationary point. The results are summarized below in Table S1. Minimal structural differences were observed between the presence and absence of the solvent field. As the implicit solvation model did not greatly impact the structure and due to computational costs, only gas phase optimizations are presented for all complexes to evaluate the impact of explicit solvent-solute interactions.

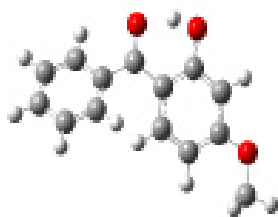
Table S1: Calculated B3PW91/Midi! geometries for the DOB:MeOH complex in the gas and solution (IEFPCM model for MeOH) phase. Values are for the 1:1 complex with bonding at the phenyl group without the methoxy substituent.

		gas	solution
Dioxybenzone: MeOH complex <sup>a</sup>	$\alpha_1$	1.558	1.554
	$\alpha_2$	2.677	2.669
	$\beta_1$	1.676	1.675
	$\beta_2$	1.545	1.543
	$\theta_1$	152.8	152.8
	$\theta_2$	100.8	100.8
	$\theta_{\text{HB}}$	155.7	155.3
		172.2	172.5
	$\Theta$	53.1	53.6

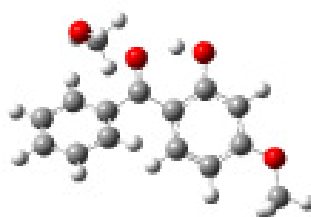
a. Figure 6 illustrates measurements and complexes of interest. Bond lengths are given in Ångstroms and angles in degrees.

### Solvent-Solute Optimized Geometries

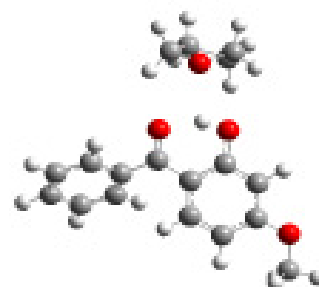
OB



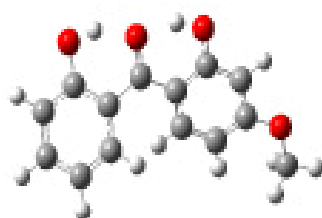
OB:MeOH



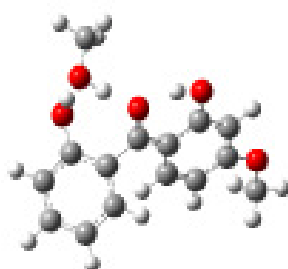
OB:THF



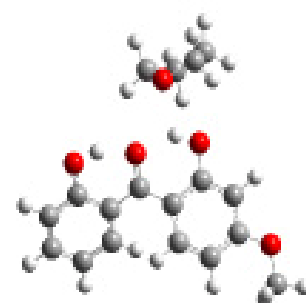
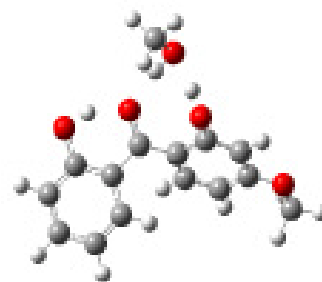
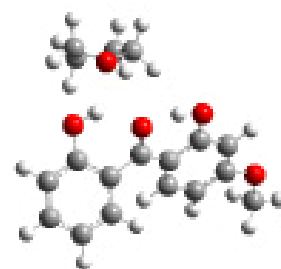
DOB



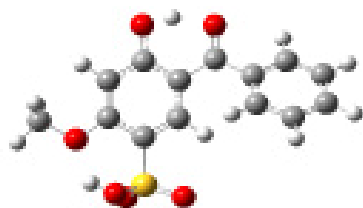
DOB:MeOH



DOB:THF



SB



SB:THF

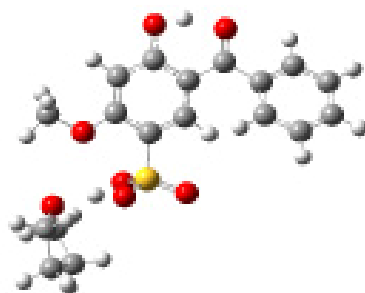


Figure S1: Representative B3PW91/Midi! optimized structures of the free and 1:1 solute:solvent complexes of the benzophenones. Acetonitrile complexes resemble those of THF and sulisobenzene complexes at the hydroxyl position are analogous to those of oxybenzone.

## Comparison of $S_1$ and $S_2$ absorbance bands

Calculated oscillatory strengths and experimental integrated absorbance bands were compared to assess the relative intensities of the first ( $S_0$  to  $S_1$ ) and second ( $S_0$  to  $S_2$ ) electronic transitions. The ratios of the first to second transitions are compared below in Table S2. The calculated values are determined as the direct ratio of the oscillatory strength for the first transition relative to the second transition, as determined in ArgusLab. The experimental value is found by fitting the experimental spectra as two gaussian curves, in OriginPro, and evaluating the ratio of the areas for the first and second absorbance bands that compose the spectra presented in the article. Experimentally toluene (OB and DOB) or hexanes (SB), methanol, and acetonitrile were examined to represent the three solvent classes. Computationally the oscillatory strengths were evaluated for the gas phase, as well as with methanol or acetonitrile solvation, using ZINDO calculations in ArgusLab. The oscillatory strengths were also evaluated for the explicit solvent:solute complexes both in the gas phase and relevant solvent environment.

The calculated values are generally higher than the experimental values, and solvents do not greatly alter the observed ratios. The experimental spectrum for OB (Figure 2) and SB (Figure 4) do not show significant changes in the spectral profile between the solvents. In contrast the absolute intensities for the first two absorbance bands do vary for DOB between solvents with specific interactions (electron pair donating and protic solvents) relative to those without (Figure 3). The second absorbance band increases in intensity for the former solvents. In terms the analysis presented in Table S2 this is not seen, as the increased intensity of the high energy band is accompanied by both narrowing of the band and broadening of the low energy band. The net result is minimal changes in the overall ratio of the areas of the two bands. In the calculation there is a predicted decrease in the ratio of the  $S_1/S_2$  oscillatory strengths, which correlates with the observed decrease in the absolute peak intensity of the  $S_1$  band relative to  $S_2$  in solvents which have specific solvent-solute interactions.

Table S2: Relative ratio of first and second electronic transitions for the benzophenones and complexes as determined experimentally (E) and computationally (C),  $S_1/S_2$ .

		Environment		
Solute	Type	NSI <sup>a</sup>	ACN	MeOH
OB	E	0.656	0.665	0.690
OB	C	1.027	1.460	0.998
OB:MeOH	C	1.008	---	0.865
OB:ACN	C	1.009	1.568	---
DOB	E	1.012	1.030	1.093
DOB	C	2.410	2.050	1.698
DOB:MeOH	C	2.655	---	1.562
DOB:ACN	C	2.658	2.157	---
SB	E	0.427	0.726	0.538
SB	C	0.803	0.677	0.811
SB:MeOH	C	0.699	---	0.622
SB:ACN	C	0.700	0.574	---

a. NSI = no specific interaction; experimentally hexanes or toluene, and computationally gas.