



**ENGINEERING CRYSTALS FOR EXCITED STATE DIFFRACTION STUDIES:
STRUCTURE AND SPECTROSCOPIC PROPERTIES OF TWO POLYMORPHIC
MODIFICATIONS OF THE 4,4'-DIHYDROXYBENZOPHENONE/
4,13-DIAZA-18-CROWN-6 COMPLEX**

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ABSTRACT

The crystal structures of two modifications of 4,4'-dihydroxybenzophenone with 4,13-diaza-18-crown-6 have been analyzed in terms of their suitability for time-resolved diffraction studies of transient excited species in crystals. The room-temperature lifetimes of the triplet excited state of the dihydroxybenzophenone molecule in the two modifications have been determined as $44.2 \pm 1.2 \mu\text{s}$ and $49.2 \pm 0.5 \mu\text{s}$ in the monoclinic and triclinic forms, respectively. © 1999 Elsevier Science Ltd

KEYWORDS: excited state diffraction studies, triplet state lifetime, dihydroxybenzophenone

INTRODUCTION

With the advance of very bright third-generation synchrotron sources, analysis of the structure of excited states of molecules is becoming a realistic possibility. It is therefore necessary to identify systems suitable for such studies [1].

The lifetimes of molecular excited states are typically in the msec- μ sec range in the case of triplet states and nsec or less for singlet states. With such short lifetimes it is not possible to build up an appreciable steady state concentration of excited state molecules. It is therefore necessary to use non-equilibrium methods based on synchronization of pump and probe

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sources. The pump-probe experiments presently envisioned will use a pulsed laser beam synchronized to the time-structure of a pulsed X-ray source.

To obtain a reasonable population of excited state molecules in the crystal, the number of photons per laser pulse must be of the same order of magnitude, or larger, than the number of photo-active molecules in the crystallite being used for the analysis. While a large conversion percentage is desirable, it raises the probability that the crystal will disintegrate because of changes in the molecular shape, and it may reduce excited state lifetimes as a result of exciton–exciton annihilation. It is further desirable to minimize the energy to be dissipated in the crystal. For such reasons, it is essential to use crystal engineering in order to reduce the number of photo-active molecules per unit volume. This may be done by including a second, photo-inactive component in the crystals.

We describe here two modifications of a binary solid, which are candidates for the excited state diffraction experiments. The photo-active component is a dihydroxy derivative of benzophenone, the spectroscopic properties of which have been studied extensively since the late 1960s [2]. Of particular interest for the current purpose is the T_1 triplet state generated by an (n,π^*) transition, which reportedly has a lifetime of the order of microseconds [3] and is an important intermediate in a number of photochemical reactions [4]. The structural change upon excitation to the triplet state was calculated by Hoffmann and Swenson, using Extended Hückel and CNDO/2 methods [5]. The calculations predict that the torsion angles of the two benzene rings around the exocyclic C–C bond are reduced from 38° in the ground state to about 32° in the excited state. Later analysis of the vibrational spectra of the excited state showed that the C=O bond stretching frequency in the T_1 state is typical for a single bond, and thus that the C=O bond is considerably weakened, and that the π^* electron is likely delocalized on the aromatic rings [4].

Several complexes of organic molecules with 4,13-diaza-18-crown-6 (1,4,10,13-tetraoxa-7,16-diaza-cyclooctadecane, Reg. #[23798-55-4]) have been described in the literature [6,7, 8,9]. The complex of 4,4'-dihydroxybenzophenone with 4,13-diaza-18-crown-6 crystallizes in two polymorphic modifications. Their structures were determined at 20 K using synchrotron radiation and the spectroscopic properties of the crystals are described below.

EXPERIMENTAL

Crystal Growth

Crystals were grown from a 1:1 solution of 4,4'-dihydroxybenzophenone and 4,13-diaza-18-crown-6 in ethyl acetate. All chemicals used were obtained from commercial sources. Crystals of the triclinic phase were grown by slow evaporation of the solvent at room temperature. More rapid evaporation, achieved by warming the solution or increasing the exposed surface area, led to formation of the monoclinic phase. While the monoclinic crystals are needle-shaped, the triclinic specimens are approximately equidimensional in all directions. The 1:1 ratio of 4,13-diaza-18-crown-6 and 4,4'-dihydroxy-benzophenone in both phases was confirmed by ^1H NMR and by the subsequent X-ray analysis.

X-ray Diffraction

X-ray data were collected at the SUNY X3A1 beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, using a $\lambda = 0.643 \text{ \AA}$ X-ray beam. Fuji imaging plates were used as detectors. For data collection, the crystals were cooled to 20 K

TABLE 1
Crystallographic Data

	Triclinic Modification	Monoclinic Modification
Compound name	Dihydroxybenzophenone-diaza-18-crown-6	
CCDC deposit no.	CCDC-1294/72	CCDC-1294/73
Chemical formula	$C_{25}H_{36}N_2O_7$	
Formula weight	$M_r = 476.56$	
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Temperature, K	20 (2)	20 (2)
a , Å	8.620 (1)	8.913 (1)
b , Å	10.269 (1)	17.501 (1)
c , Å	15.717 (1)	17.110 (1)
α , deg	90.59 (1)	90.0
β , deg	104.28 (1)	104.23 (1)
γ , deg	111.20 (1)	90.0
Volume, Å ³	1249.4 (2)	2587.0 (4)
Z	2	4
ρ_{calcd} , g cm ⁻³	1.267	1.224
Absorption coefficient μ , mm ⁻¹	0.092	0.085
R	0.037	0.044
wR_2	0.122	0.107

in a Displex cryostat. No phase transitions were observed on cooling of either of the phases. Data collection details, crystallographic information, and information on the refinements are summarized in Table 1. The structures were solved by direct methods with SHELXTL and refined with SHELXL-97. Packing diagrams are shown in Figs. 1 and 2.

DSC Experiment

The melting behavior of the two phases was studied by differential scanning calorimetry (DSC), using a Perkin Elmer calorimeter. Scan speeds of 2–5°/min were used.

Spectroscopic Results

Several small crystals of each of the modifications were sandwiched between two quartz plates. The experiments were performed at room temperature. Static excitation and emission scans and the excited state luminescence decay curves were recorded. An SLM 48000 spectrofluorometer was used to acquire the static spectra, and an N₂ laser-based system ($\lambda_{\text{ex}} = 337$ nm) served for the excited state experiments [10]. The observed excitation maxima for both modifications peaked at 345–355 nm excitation. The emission spectra of the two phases, shown in Fig. 3, are virtually identical.

For both phases the luminescence decay kinetics follows a single exponential decay law ($I(t) = \exp(-t/\tau)$). The room-temperature lifetimes (τ) obtained from a fit to the data are equal to 44.2 ± 1.2 μs and 49.2 ± 0.5 μs for the monoclinic and triclinic phases, respectively. Thus, there appears to be a slight but significant difference between the two phases.

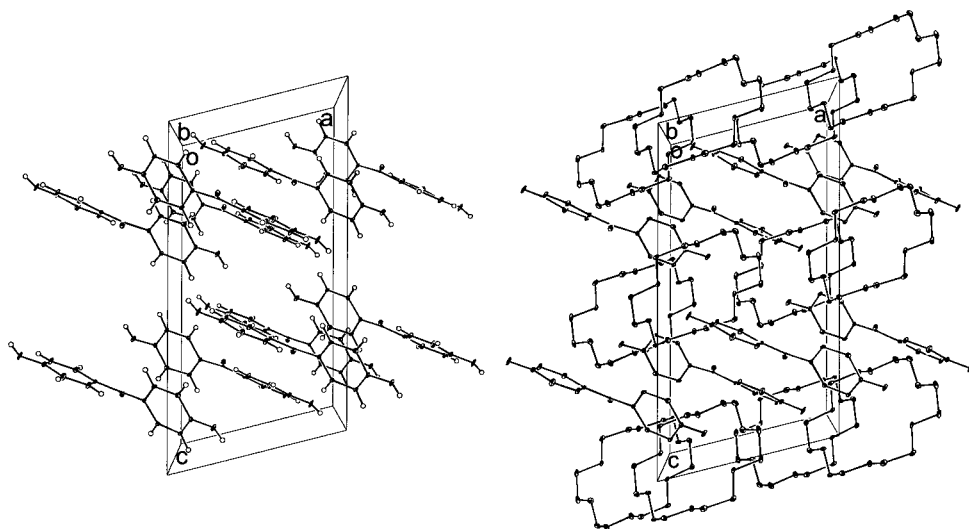


FIG. 1

Packing diagram of the monoclinic structure: (a) dihydroxybenzophenone molecules only; (b) both components, hydrogen atoms omitted.

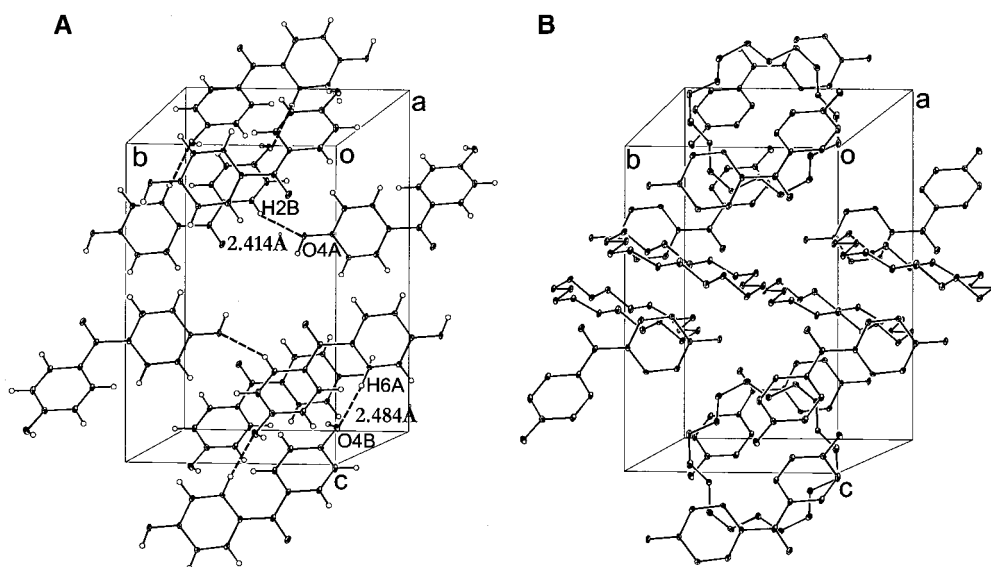


FIG. 2

Packing diagram of the triclinic structure: (a) dihydroxybenzophenone molecules only; (b) both components, hydrogen atoms omitted.

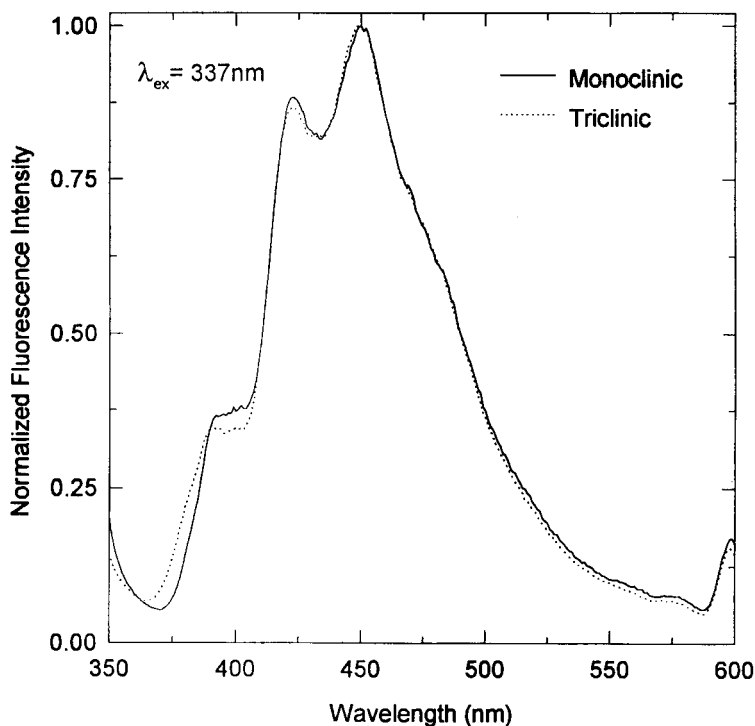


FIG. 3

Normalized room-temperature luminescence emission profiles of dihydroxybenzophenone in the monoclinic and triclinic phases.

DISCUSSION

Relative Stability of the Two Polymorphs

The fact that the monoclinic polymorph is formed on rapid evaporation of the solution, while the triclinic phase crystallizes on slow evaporation, suggests the latter to be thermodynamically stable. In agreement with this, the triclinic phase has the higher density (1.267 g/cm^3 vs. 1.224 g/cm^3 for the monoclinic modification), thus suggesting more efficient packing. The DSC curves show the monoclinic phase to melt in the $132\text{--}135^\circ\text{C}$ region with maximum heat dissipation at 133.8°C . For the triclinic modification, however, the behavior is more complex, as two peaks at 128.8 and 133.0°C are observed. The presence of both phases in the triclinic sample can be ruled out, as a single crystal specimen was used. As the second peak is only about 10% of the intensity of the first peak, this suggests a premelting to an intermediate, strongly disordered phase, or perhaps a partial conversion of the triclinic to the monoclinic phase. However, the latter interpretation would imply the monoclinic phase to be the stable form, which is not in agreement with the other evidence.

Comparison of the Two Structures

The dominant packing feature of both phases is hydrogen bonding between the OH groups of dihydroxybenzophenone and the nitrogen atoms of the diaza-crown ether molecules. In the

TABLE 2
Twist Angles ($^{\circ}$)^a in Benzophenone and Dihydroxybenzophenone

	Ring A	Ring B	Reference
Benzophenone	31.0	28.7	[12]
	30.8	30.0	[13]
Dihydroxybenzophenone			
mol 1	31.8	21.0	[14]
mol 2	30.2	20.7	
Monoclinic phase	41.6	14.4	This study
Triclinic phase	35.2	16.2	This study

^aDefined as the angle between the CC = OC plane and the plane of the phenyl ring. Least squares planes calculated with PLATON [15].

monoclinic phase, the corresponding hydrogen bond distances are 2.678(2) and 2.639(2) Å, and the O–H...N angles are 176(3) and 173(3) $^{\circ}$, respectively. The corresponding values for the triclinic phase are 2.714(2) and 2.665(1) Å and 176(2) and 168(2) $^{\circ}$, thus indicating slightly weaker H-bonding in the triclinic phase. In both modifications the angles between each of the phenyl rings and the plane through the central CC=OC atoms differ considerably from each other (Table 2). In both forms one of the torsion angles is close to the benzophenone gas phase value of 40–45 $^{\circ}$ [11], while the twist angle for the other ring is much smaller than observed elsewhere. Detailed examination of the bond lengths shows the exocyclic C–C bond and the C–C bonds parallel to the long axis of ring to be shorter by about 0.01 Å for the less distorted ring, indicating a slight quinoid character of the former in both modifications.

In the monoclinic structure, the benzophenone molecules are separated from each other by the host molecules. In the triclinic structure, there are two contact distances of 2.41(2) and 2.48(2) Å (using X-ray positions for the hydrogen atoms) respectively, between hydroxyl oxygen atoms and ortho hydrogen atoms in adjacent benzophenone molecules, as shown in

TABLE 3
Shortest Distances (Å) Between Benzophenone Carbonyl Oxygen Atoms in a Number of Solids

Benzophenone [10]	Dihydroxybenzophenone [11]	Monoclinic Modification [This Study]	Triclinic Modification [This Study]
6.04 (2 \times)	4.75 (2 \times)	8.6 (2 \times)	6.40
6.35 (2 \times)	4.76	8.91 (2 \times)	7.75
7.10 (2 \times)	4.85	9.53 (2 \times)	8.62 (2 \times)
7.80 (2 \times)	6.35	10.14 (2 \times)	9.13
8.00 (2 \times)	7.28 (2 \times)	10.74 (2 \times)	10.08

Number of contacts per carbonyl group appears in parenthesis.

Fig. 2. While the shortest C=O...O=C distance in a neat benzophenone crystal is 6.04 Å, it is 6.401(2) Å in the triclinic modification of the diazacrown complex, and as high as 8.5654(5) Å in the monoclinic form (Table 3).

The comparatively long lifetime of the T₁ triplet excited state of benzophenone has been attributed to the separation of the carbonyl oxygen atoms, at which the n to π* excitation is roughly localized, in the crystals of benzophenone [2]. At higher triplet state concentrations, the excited state lifetime will be shortened by triplet-triplet annihilation, which depends on the separation of the excitation centers. This would suggest that crystals of the monoclinic form are more suitable for the excited state diffraction studies, as relatively high conversion percentages are required. Further spectroscopic studies at low temperature using intense pulsed laser sources will be performed to clarify the relative merits of the two polymorphic modifications.

CONCLUSION

Given the long room-temperature lifetime of the benzophenone T₁ state in the solid complexes with 4,13-diaza-18-crown-6 and the increased separation of the excitation centers compared with the neat crystals, the two modifications described above appear to be suitable candidates for time-resolved studies on a μsec time scale. Apart from anticipated change in the length of the C=O bond, the change in twist angle of 6° predicted by Hoffman and Swenson [5] would correspond to a movement of the 2,3,5,6 phenyl carbon atoms by about 0.1 Å, which would be readily detectable even in a partially converted crystal. It is not obvious whether the hydrogen bonding geometry is modified in the excited state crystals, or whether the H-bonds are temporarily broken, as the excited molecules do not necessarily occupy a position of lowest energy in the crystal. The answer to such questions must await completion of the experiments now under consideration.

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