with a nitrogen-degassed mixture of 7:3 CH_2Cl_2/EtOAc and with a constant stream of nitrogen passing over the collected eluent. The chromatography gave the alcohol, **14** (48 mg), as a pale yellow solid: ^1H NMR ($CDCl_3$) δ 7.14 (s, 1 H), 4.86 (d, J = 11.5 Hz, 1 H), 4.18 (d, J = 11.2 Hz, 1 H), 4.05 (d, J = 11.5 Hz, 1 H), 4.02 (d, J = 11.2 Hz, 1 H), 3.41 (d, J = 10.7 Hz, 1 H), 3.24 (s, exchanges with D_2O, 1 H), 2.33 (d, J = 10.7 Hz, 1 H), 1.33 (s, 3 H), 1.32 (s, 3 H), 1.19 (s, 3 H), 1.18 (s, 3 H); ^{13}C NMR (attached protons established with DEPT pulse sequence) δ 165.3 (C=O), 162.4 (C=O), 124.6 (vinylic CH), 111.3 (vinylic C), 79.0 (C), 75.5 (CH_2), 72.8 (CH_2), 54.2 (C), 51.6 (C), 48.9 (CH_2), 25.8 (CH_3), 24.4 (CH_3), 22.5 (CH_3), 17.8 (CH_3); IR (KBr pellet) 3379 (OH), 1756 (ester C=O), 1689 (conjugated ester C=O), 1603 cm^{-1} (C=C); UV (MeOH) λ_{max} 334 ($\epsilon = 12\,500$), 214 nm ($\epsilon = 8270$); mass spectrum (70 eV) m/z (relative abundance) 296 ($M^{\bullet+}$, 100), 281 (70), 278 (24), 181 (30), 151 (26), 123 (30), 95 (23), 78 (18), 55 (60). Calcd for $C_{14}H_{20}N_2O_5$: C, 56.75; H, 6.80. Found: C, 56.47; H, 6.81.

Further elution gave a crystalline, violet solid (113 mg) containing the tetrahydropyrazine derivative **13** and the corresponding radical cation **16**, responsible for the violet color, λ_{max} 562 (CH_3CN) and 612 nm (HOAc), and having an ESR spectrum in oxygen-free THF as shown in Figure 2.

4a,8a-Diaza-2,6-dioxa-3,4,7,8,9,9a-hexahydro-9,9a-(1′-phenyl-2′,5′-dioxo-1′,3′,4′-triazoline-3′,4′-diyl)-4,4,8,8-tetramethylanthracene-1,5-dione (17). Under a nitrogen atmosphere, 139 mg of DDTTA was added to a solution of 88 mg of 1-phenyl-1,3,4-triazoline-2,5-dione (PTAD) in 20 mL of dichloromethane. The deep color of the solution faded after approximately 1 min to a pale yellow. Evaporation of the solvent gave an orange glass that was purified by filtration through a silica gel column using 9:1 dichloromethane/ethyl acetate (v/v) as solvent. Evaporation and recrystallization from dichloromethane/heptane gave pale yellow needles (120 mg, 53%): mp 170 °C dec; ^1H NMR ($CDCl_3$) δ 1.18 (s, 6 H), 1.34 (s, 3 H), 1.57 (s, 3 H), 4.05 (d, J = 10.8 Hz, 1 H), 4.06 (d, J = 11.6 Hz, 1 H), 4.19 (d, J = 11.6 Hz, 1 H), 4.36 (J = 10.8 Hz, 1 H), 6.35 (s, 1 H), ~7.5 (m, 5 H), 7.65 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 160.0, 153.3, 152.9, 151.3, 146.2, 129.4 (2 C), 128.6, 125.2 (2 C), 113.2, 110.6, 77.8, 74.1, 65.5, 55.9, 55.2, 25.5, 23.3, 21.7, 21.4; IR (KBr) 1781 (C=O), 1734 (C=O), 1627 cm^{-1} (C=C); mass spectrum (70 eV) m/z (relative intensity) 453 ($M^{\bullet+}$, 15), 327 (6), 278 (100), 223 (16), 178 (32), 151 (25), 119 (39). Measurement of the exact mass of the molecular ion gave m/z = 453.1632 (calcd for $C_{22}H_{22}N_5O_6$, m/z = 453.1648); **17** could not be obtained pure enough for elemental analysis.

Acknowledgment. We thank the NSF for financial support in the form of Grants CHE-8903637 and CHE-9201075, Dr. Cortlandt Pierpont for use of his cyclic voltammetry apparatus, and Dr. Makhluf Haddadin for suggesting the reaction with PTAD. D.J.R.B. also gratefully acknowledges financial support in the form of the Perry and Margie Argabright Fellowship at the University of Colorado.

Supplementary Material Available: A complete description of the X-ray crystallographic determination of the trifluoroacetate salt of DDTTA including atomic coordinates, isotropic and anisotropic displacement parameters, bond lengths, and bond angles (11 pages); listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

Norrish II Reactions of Liquid-Crystalline Ketones. Comparison between Smectic B and Solid Phase Order and Control of Photoproduct Distributions[1]

Inna Furman,[†] Raymond J. Butcher,[‡] Robert M. Catchings,[§] and Richard G. Weiss*,[†]

Contribution from the Department of Chemistry, Georgetown University, Washington, D.C. 20057, and Departments of Chemistry and Physics and Astronomy, Howard University, Washington, D.C. 20059. *Received December 18, 1991. Revised Manuscript Received March 16, 1992*

Abstract: The Norrish II photoreactions of *trans*-1-(4-heptanoylphenyl)-4-heptylcyclohexane (**2a**) and *trans*-1-heptyl-4-(4-nonanoylphenyl)cyclohexane (**2b**) have been examined in their isotropic, smectic B, and solid phases. The smectic phases have been characterized by optical microscopy, differential scanning calorimetry, and X-ray diffraction. Solid and smectic phase order, probed by deuterium NMR spectroscopy of **2** deuteriated at the methylene α to the carbonyl group, is correlated with the photochemical results. The apparent absence of a directing influence of the smectic B phases on the course of the Norrish II reactions of **2** is attributed to the local fluidity afforded the methylene groups of the alkyl chains. The solid phase influence on the distribution of Norrish II photoproducts is significant and indicates that a small amount of motional freedom persists in the alkyl chains even after bulk crystallization.

Introduction

Liquid-crystalline phases can provide constrained environments capable of directing the motions, conformations, and reactions of appropriately designed solute molecules.[2] For example, the structural link between ketones in nematic, smectic, and solid phases of mesogenic hosts and their Norrish type II photoreactions have been extensively investigated.[2] Recently, we reported the results from a study of the Norrish II reactivity of two neat liquid-crystalline ketones (**1a** and **1b**, Scheme I) in their isotropic, nematic, and solid phases.[3] In such systems, the disturbances that a foreign solute may impose on the packing order of its anisotropic host molecules are absent; in principle, any selectivity detected in reactions of molecules in a neat phase may be attributed to restrictions imposed by the undisturbed host lattice.

Herein, we report the Norrish II photoreactivity (Scheme I) of *trans*-1-(4-heptanoylphenyl)-4-heptylcyclohexane (**2a**) and *trans*-1-heptyl-4-(4-nonanoylphenyl)cyclohexane (**2b**) in their isotropic, smectic B, and solid phases. The elimination to cyclization (E/C) product ratios are used to measure the influence of phase order on the course of the reaction. In this study, selectivity is defined as the ratio of E/C values in the anisotropic

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[†] Georgetown University.

[‡] Department of Chemistry, Howard University.

[§] Department of Physics and Astronomy, Howard University.

(1) Part 45 in our series, Liquid-Crystalline Solvents as Mechanistic Probes. Dedicated to Prof. K. Venkatesan on the occasion of his 60th birthday. For Part 44, see: Weiss, R. G.; Chandrasekhar, S.; Vilalta, P. M. *Collect. Czech. Chem. Commun.*, submitted for publication.

(2) For reviews, see: (a) Weiss, R. G. *Tetrahedron* **1988**, *44*, 3413. (b) Weiss, R. G. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH: Weinheim, 1991; Chapter 14 and references therein.

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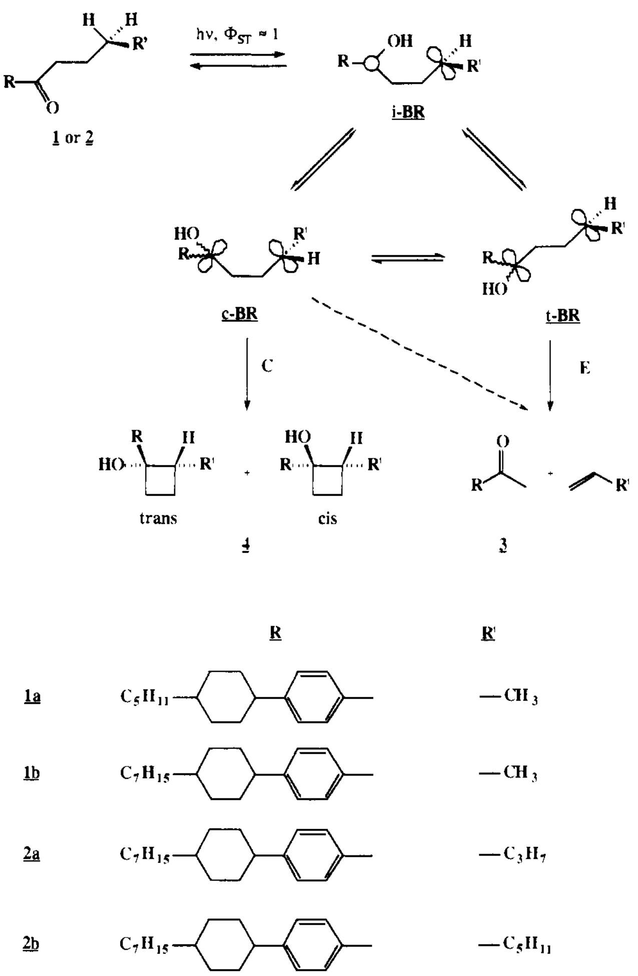
Scheme I. The Mechanism of the Norrish II Photoreaction Showing the Biradical Precursors of **3** and **4**[a]



[a] Each **BR** includes a family of related conformations which are precursors of a product or process.

and isotropic phases. The photoproduct ratios are supplemented with data (from optical microscopy, differential scanning calorimetry (DSC), X-ray diffraction and deuterium NMR spectroscopy on **2a** and **2b** deuteriated at the methylene α to the carbonyl groups) which permit the nature of the phases and the lability of molecules within them to be ascribed.

The results demonstrate that in considering the influence of smectic phase order on the course of the Norrish II process, the environment afforded to the locus of reaction must be considered in addition to the macroscopic phase order as a whole. Photolysis results for solid **2**, when compared to Norrish II E/C ratios obtained for appropriately designed ketones dissolved in host solid lattices,[4-6] indicate that the neat phases may be less restrictive than some of the ones with solid solutions.

Results and Discussion

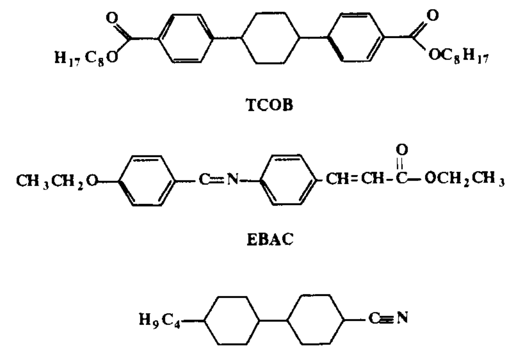
Optical Microscopy and Differential Scanning Calorimetry. The phase transition temperatures and the associated heats of transition for **2**, as determined from differential scanning calorimetry, are shown in Figure 1. Ketones **2a** exhibit two solid phases: the lower temperature solid, KI, is the phase obtained by recrystallization from ethanol; heating KI transforms it into KII; upon standing at room temperature, KII reverts to KI. Two solid phases of **1** were also detected.[3] Typical heating and cooling thermograms for **2** are included in Figure 1. They are reproducible in subsequent scans except for the KI-to-KII transition. Protracted annealing times are required to convert KII to KI after cooling.

Table I. X-ray Diffraction Data from **2**

	2θ (deg)	D (Å)	d (Å)	molecular length (Å)[a]
2a	3.82		23.1	24.4
	18.88	5.42		
	19.17	5.34		
2b	3.60		24.6	26.7
	19.13	5.32		
	19.39	5.28		

[a] Calculated using the Chem-X program.[11]

Chart I



The mosaic texture of the smectic phase of **2a**, obtained on cooling from the isotropic phase (Figure 2a), is characteristic of the smectic B phase.[7] The enantiotropic region of this phase persists for only 1.5 °C while the monotropic region extends over 25 °C. The birefringent textures of the smectic phase of **2b**, formed by heating from the solid (Figure 2b) and by cooling from the isotropic phase (Figure 2c), are reminiscent of the smectic B phase of 1,4-bis(4-*n*-pentylphenyl)cyclohexane.[8] The **2b** smectic B phase is enantiotropic over a 10 °C range and monotropic over 25 °C. Prior to crystallization, it undergoes a phase transition to another smectic modification whose arced focal conic fan texture is indicative of a smectic E phase (Figure 2d).[8]

X-ray Diffraction. Unfortunately, we have been unable to grow single crystals of either homologue of **2** that are satisfactory for X-ray structural analysis. On the basis of the solid state structure of somewhat related molecules, *trans,trans-4′-n-alkyl*[1,1′-bicyclohexyl]-4-carbonitriles,[9] the alkyl chains of **2** are expected to be in fully-extended conformations and the molecules should pack in layers in their solid phases.

The smectic phases of the ketones could be characterized further by X-ray diffraction. The powder diffraction patterns from the smectic phases of **2** are shown in Figure 3 and the data obtained from them are summarized in Table I. The low angle diffraction peak is attributed to the layer thickness of the phase (d) and has been calculated with use of Bragg's law.[10] For both compounds, d corresponds to the van der Waals molecular length calculated by the Chem-X package.[11] This demonstrates that the long molecular axes are orthogonal to the smectic layer planes. In the smectic phases of **2a** and **2b**, the intensities from the low angle peaks are larger when the sample is cooled from the isotropic phase than when it is heated from its solid; compare, for example, Figure 3, b and c. This behavior is attributed to the partial alignment of the molecules with respect to the sample plate, which is induced by cooling from the isotropic phase.

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(11) Geometry subroutine of Chem-X, Chemical Design, Ltd., 1991. The program assumes that the Van der Waals radius is $^{3}/_{5}$ of the CPK radius.

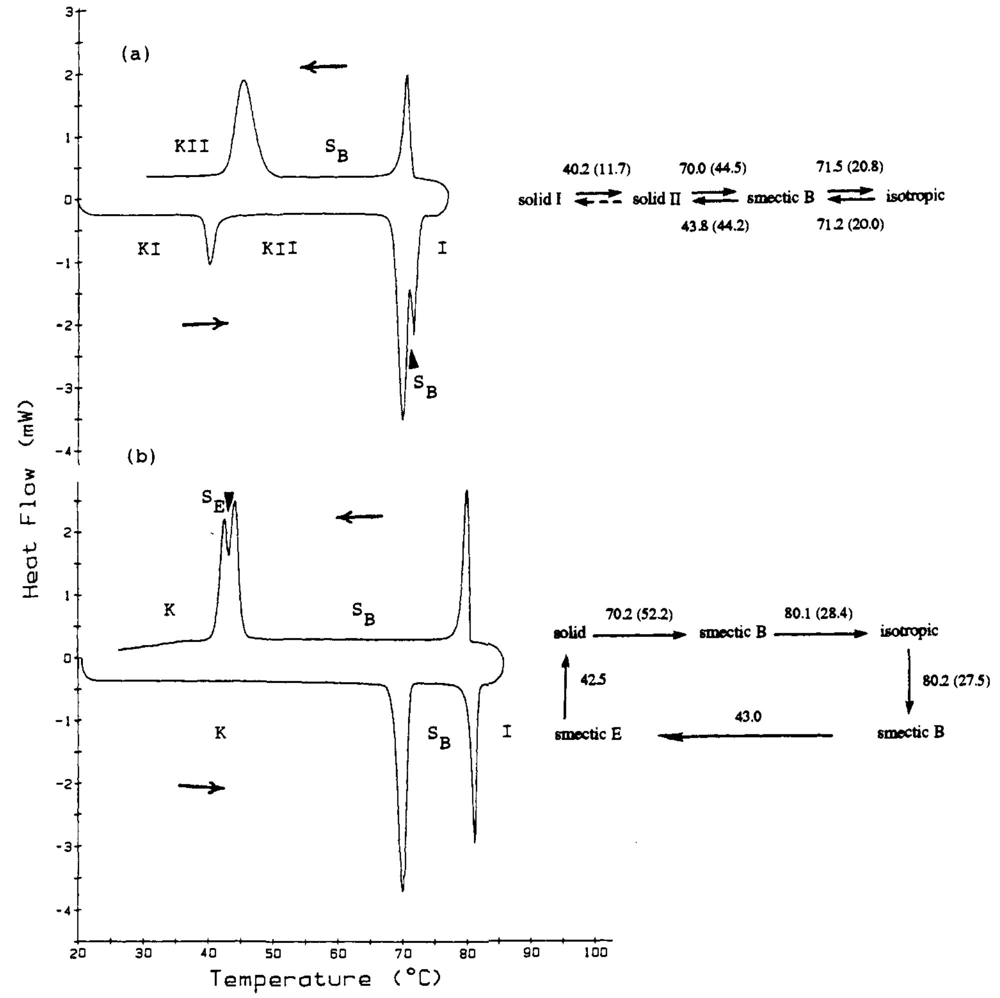

Figure 1. Differential scanning calorimetry thermograms from heating and cooling of (a) **2a** and (b) **2b** at 2 °C/min. Phase transition temperatures (°C) and heats of transition (J/g) in parentheses from heating and cooling of **2a** and **2b** are also included. Due to the overlap of the S_B and S_E transitions for **2b**, the exact heats of transition for each could not be determined. The total heat of the smectic to solid transition on cooling from the isotropic phase for **2b** is 50.9 J/g.

The high angle peaks ($2\Theta = 18.9$–$19.4°$) correspond to the intermolecular distances (D) within smectic layers. In Table I, these values have been calculated with use of a modified version of Bragg's law (eq 1), which takes into account the hexagonal

$$2D \sin \Theta = 1.1547\lambda \qquad (1)$$

packing arrangement within the layers.[12] In eq 1, D is the intermolecular distance and λ is the wavelength of radiation used (1.5406 Å).

The average distance between molecules of **2** within a smectic layer is 5.3 Å. *trans*-1,4-Cyclohexanediyl-4,4′-bis(*n*-octyl benzoate) (**TCOB**), which possesses the same phenylcyclohexyl core as **2**, has a calculated intermolecular distance of 5.3 Å in its smectic B phase.[12] This is significantly larger than the average intermolecular distances of 4.9–5.0 Å[10] in the smectic B phases of compounds that contain only phenyl cores (for example, ethyl 4-((4-ethoxybenzylidene)amino)cinnamate (**EBAC**), $D = 4.85$ Å[9]); it is smaller than the 5.7 Å observed from the smectic B phase of *trans,trans*-4′-butyl[1,1′-bicyclohexyl]-4-carbonitrile (**BCCN**).[13] The trend noted among the three types of smectic B liquid crystals and their interatomic distances can be rationalized by the fact that a nonplanar cyclohexyl ring occupies a larger volume than a planar phenyl group.[12]

As a consequence of the apparent lack of chain interdigitation and the relatively large intermolecular distance between core groups of smectic **2**, their long alkyl chains should exist in an environment which includes significant free volume and, therefore, should impose minimal constraints upon motions of methylene groups near chain ends. The looseness of chain packing in the smectic phase of **2** should effectively prevent interlayer correlations that have been observed in other smectic B phases.[14] That the alkyl chains are not forced into fully extended conformations in the smectic phase is demonstrated further by the d values which are slightly smaller than the molecular lengths (Table I).

The presence of the sharp high angle peaks ($2\Theta = 18.9$–$19.4°$) in the diffractograms of the smectic phases of **2** is attributed to the well-ordered phenylcyclohexyl cores. A small deviation from hexagonal packing in the smectic core leads to slightly different intermolecular distances which can give rise to two closely-spaced and sharp peaks. The broad component superimposed on the sharp high-angle peaks is attributed to the intermolecular distances between the disordered alkyl chains. A similar high-angle diffraction pattern has been observed for the smectic B phase of **TCOB**.[12] A further consequence of deviation from hexagonal packing is the appearance for **2b** of weak peaks at $2\Theta = 9.48$ and 12.58° (see Figure 3, b and c). The high-angle peaks of **2b** are indexed as (210) and ($2\bar{1}0$) in a monoclinic cell where $a = 10.58$ Å, $b = 9.32$ Å, and $c = 24.6$ Å, $\alpha = \beta = 90.0°$, $\gamma = 91.0°$. In the underlying pseudohexagonal subcell ($a = b \sim 5.29$ Å; $\gamma = 120°$), these reflections are indexed as (100) and ($1\bar{1}0$). The weak peaks, corresponding to $d = 9.32$ and 7.03 Å are indexed as (100),

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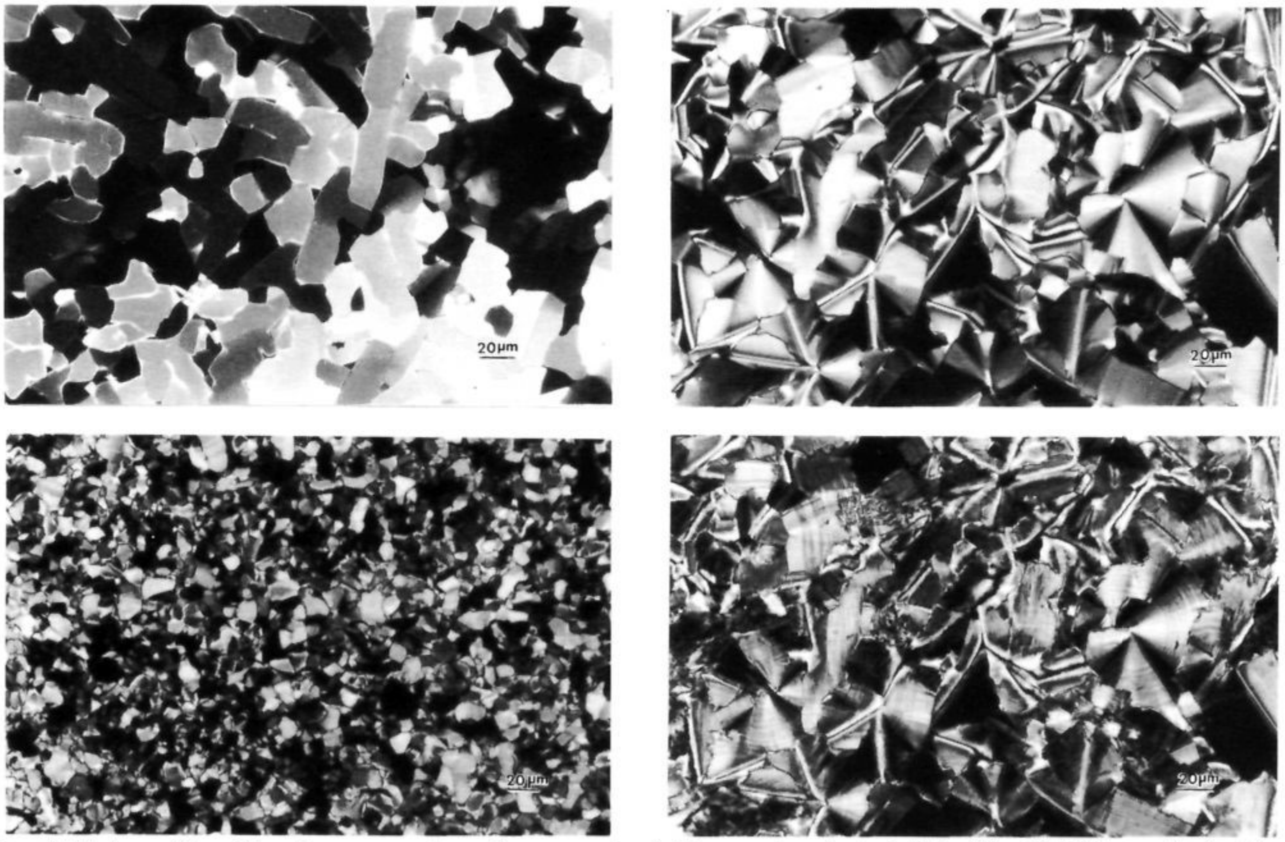

Figure 2. Textures of **2a** and **2b** as they appear under a microscope equipped with cross-polars: (a, top left) S_B of **2a** at 61.7 °C on cooling from the isotropic phase; (b, bottom left) S_B of **2b** at 78.4 °C on heating from the solid phase; (c, top right) S_B of **2b** at 58.5 °C on cooling from the isotropic phase; (d, bottom right) S_E of **2b** at 43.9 °C on cooling from the isotropic phase.

and overlapped (110) and (1$\bar{1}$0).

Deuterium NMR Spectroscopy. The ^{2}H NMR spectra of the ketones deuteriated in the methylene α to the carbonyl group are shown in their various phases in Figure 4 for **2a** and in Figure 5 for **2b**. The variation of the quadrupolar splitting ($\Delta\nu$) with temperature is plotted in Figures 6 and 7 for **2a** and **2b**, respectively. The magnitude of the quadrupolar splitting provides a measure of the restriction experienced by a C–D bond and, subsequently, the degree of phase-imposed order on the molecule as a whole.[15] In KI of **2a** and in the solid phase of **2b**, the $\Delta\nu$ values are close to the rigid molecular limit of 127.5 kHz,[16] indicating that molecular motion in these phases is severely hindered. In KII of **2a**, a greater freedom of molecular motion is evidenced by a somewhat lower quadrupolar splitting.

The smectic B phase of **2b** exhibits a Pake pattern[15] (Figure 5b) when heated from its solid phase and an aligned doublet (Figure 5d) when cooled slowly (ca. 0.5 °C/min) from its isotropic phase. In fact, the smectic B phases of both compounds align readily in the 7.0 T magnetic field of our spectrometer on cooling from the isotropic phase (Figures 4d and 5d). Considering the large degree of order known to exist in the smectic B phase, and the lack of a preceding nematic phase, it is somewhat surprising that these phases possess such a high magnetic susceptibility. The ease of alignment may be due to the relative freedom of the end alkyl chains and the large intermolecular distances within a smectic layer as determined from X-ray diffraction.

The magnetic anisotropy of **2** may be determined from the quadrupolar splittings of the aligned doublet of **2b** and its corresponding Pake pattern. As given by eq 2, $\Delta\nu$ varies with Θ, the angle between the molecular director (assumed to be the molecular z axis) and the applied magnetic field[17] (Figure 8). In eq 2, e^2qQ/h is the quadrupolar coupling constant (170 kHz for a deuterium atom bound to an aliphatic carbon atom).[15b]

$$\Delta\nu = 3/4(e^2qQ/h)\langle 3\cos^2\Theta - 1\rangle \qquad (2)$$

The inner doublet of the Pake pattern corresponds to the 90° orientation of the molecular axis with respect to the magnetic field, while the 0° orientation accounts for the outer maxima. The $\Delta\nu$ of the aligned doublet is ca. 85 kHz which corresponds to $\Delta\nu_0$ of the Pake pattern of 85.9 kHz. The ketones **2** thus align with the applied magnetic field, exhibiting a positive magnetic anisotropy.[15c] Likewise, both of the nematic **1**, deuteriated at the methylene α to the carbonyl group, align readily with the magnetic field.[3] Due to the lower order and viscosity of nematic phases, prior heating to the isotropic phase is not required to align them.[3]

The magnitude of the quadrupolar splittings obtained in both smectic B phases indicates that the deuterons on the methylene α to the carbonyl group experience a large degree of phase order and that their molecular motion is restricted. The magnitude of $\Delta\nu$, 83–88 kHz, may be compared to the 45–60 kHz obtained for the analogous deuterons on the methylene carbon β to the biphenyl group in the smectic A phase of 4-*n*-octyl-4′-cyanobiphenyl (**8CB**).[18] The smaller $\Delta\nu$ of the smectic A deuterons reflects the lower orientational order of neighboring molecules in a smectic A phase. It should be remembered that constraints imposed upon the motion of carbon atoms *at least* δ with respect to the carbonyl group determine the selectivity of the Norrish II reactions of **2**. In the nematic phases of **1**, the quadrupolar splittings for the deuterium atoms on the methylene α to the carbonyl group, 32–48 kHz,[3] are consistent with the order of the nematic phase being lower

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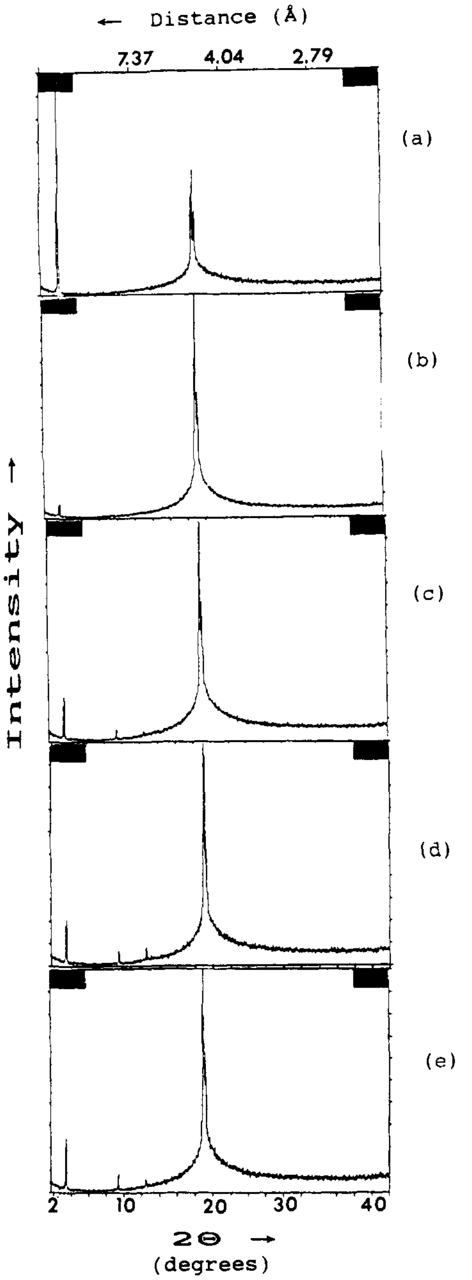

Figure 3. X-ray diffractograms from the smectic phases of **2a** and **2b**: (a) S_B of **2a** at 65 °C on cooling from the isotropic phase; (b) S_B of **2b** at 78.9 °C on heating from the solid phase; (c) S_B of **2b** at 80.0 °C on cooling from the isotropic phase; (d) S_B of **2b** at 69.9 °C on cooling from the isotropic phase; (e) S_B of **2b** at 59.9 °C on cooling from the isotropic phase. The X-ray dosage of each sample at each angle is the same.

than that of the smectic B phase. Nematic phases possess one degree of orientational order—the molecules are arranged with their long axes roughly parallel to one another. The additional degree of translational order in smectic phases by the arrangement of molecules into layers[2a] attenuates the motional freedom of the alkyl chains.

As temperature is decreased in the smectic phase of **2a** and **2b**, the magnitude of the $\Delta\nu_0$ increases slightly due to thermal damping of methylene chain motions. From the quadrupolar splitting of the aligned doublet, the order parameter, S_{zz},[19] may be obtained. Since $S_{zz} = 1/2(3\cos^2\Theta - 1)$,[19] it can be calculated by modification of eq 2, if it is assumed that the quadrupolar interaction is axially symmetric. Depending upon the sign of the magnetic anisotropy of **2** and the average orientation of its C–D bonds with

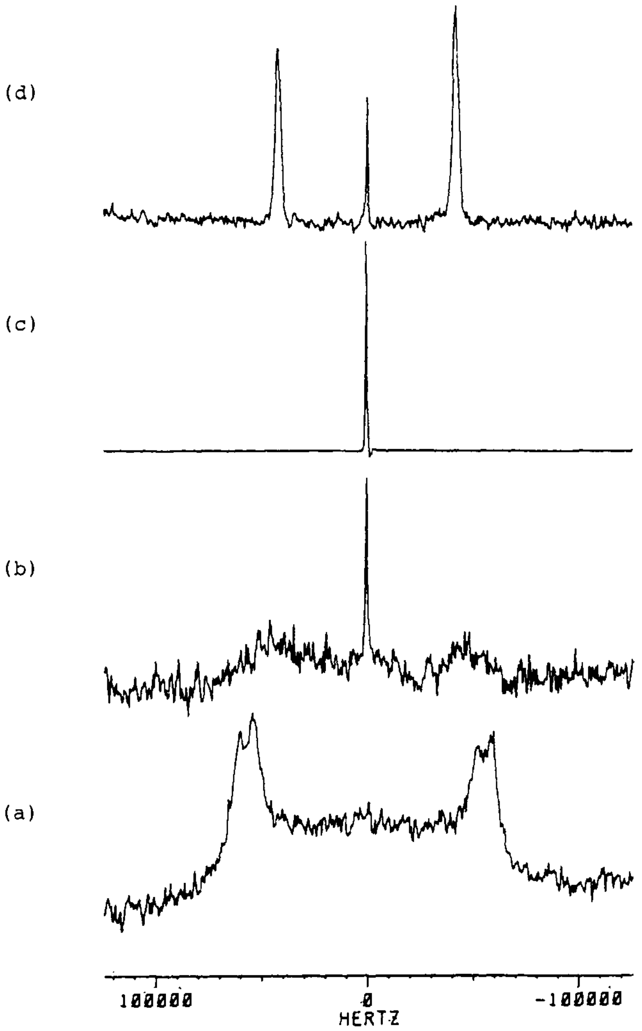

Figure 4. Deuterium NMR spectra of **2a**: (a) KI, 25 °C; (b) KII, 51 °C; (c) isotropic, 82 °C; (d) aligned S_B, 56 °C on cooling from the isotropic phase. The relaxation delay is 10 s for (a) and (b) and 1 s for (c) and (d).

respect to a defined axis system (Figure 8), S_{zz} can take values from −1 to +0.5.[19] The variation of S_{zz} which temperature in the smectic B phase of **2** is depicted in Figure 9. With the slow cooling rate used (ca. 0.5 °C/min) to pass from the smectic to the solid phase, it was possible to align partially even the solid phase of **2b** (Figure 5e). The variation of S_{zz} in smectic **2** per degree of temperature (5.3×10^{-4} per °C for **2b**) is much smaller than that reported in the nematic phase of **1** (5.7×10^{-3} per °C for **1b**)[3] since thermal motions are more limited in the smectic B phase than in the analogous nematic phase.

Irradiation of Neat 2 and Norrish II Photoproduct Ratios. The radiation was filtered through Pyrex and a Corning 0-51 cutoff filter (>30% transmittance at 380 nm). As previously described,[3] this filtering system only allows excitation of the red edge of the n–π* absorption band. At these wavelengths, the optical density of the neat **2** samples is very low, ensuring an almost equal probability for excitation of molecules throughout.

Irradiation of neat **2** results mainly in the formation of Norrish type II products. Minor side-products are detected by analytical gas chromatography, but with the low percent conversions used (<10%), these account for <1% of the converted ketone. Both diasteriomeric cyclization products (*cis-* and *trans-***4**, Scheme I) form and are analytically separable by GLC in the case of **2b**. However, the t/c values have a large precision error due to the small amount of cyclobutanol present at low percentage conversions. At higher percents of conversion, the original morphology of the neat phases can suffer serious modifications. Thus, only the E/C product ratios are reported and discussed here. The qualitative observation that the trans cyclization product is pre-

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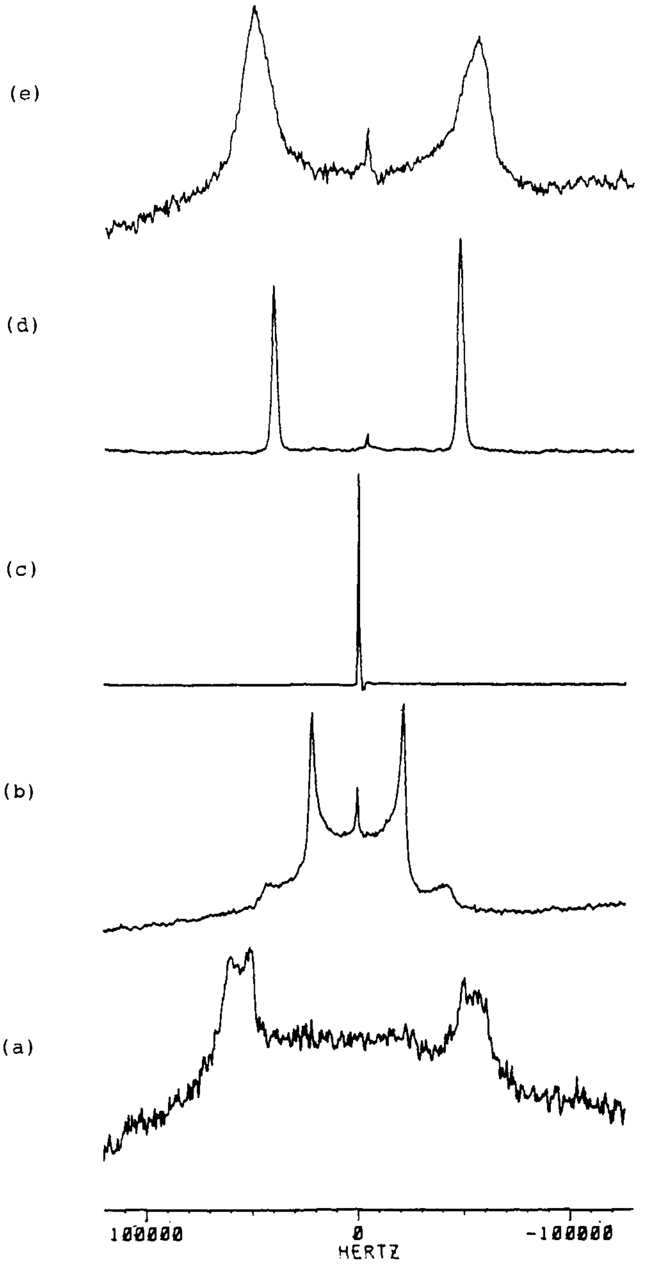

Figure 5. Deuterium NMR spectra of **2b**: (a) solid, 25 °C; (b) S_B, 72 °C on heating from the solid; (c) isotropic, 83 °C; (d) aligned S_B, 74 °C on cooling from the isotropic; (e) aligned solid, 42 °C on cooling from the isotropic.

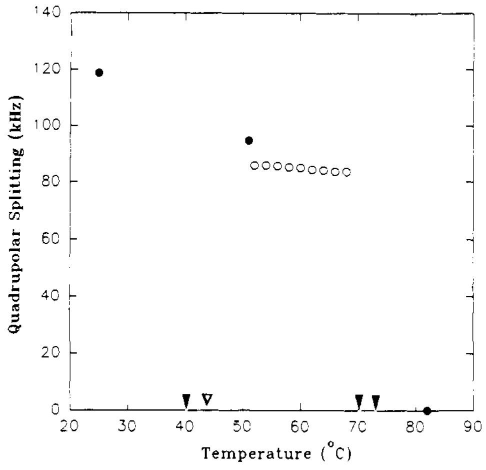

Figure 6. Quadrupolar splittings (kHz) of **2a** versus temperature (°C): (●) on heating from the solid and (○) on cooling from the isotropic phase. (▼) phase transitions on heating from the solid phase; (▽) the S_B-KII transition on cooling from the isotropic phase.

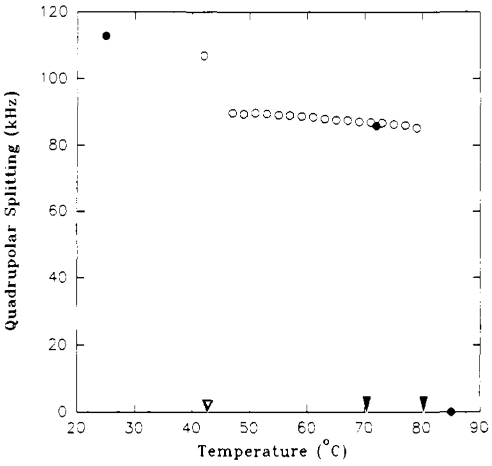

Figure 7. Quadrupolar splittings (kHz) of **2b** versus temperature (°C): (●) on heating from the solid and (○) on cooling from the isotropic phase. (▼) phase transitions on heating from the solid phase; (▽) S–K phase transition on cooling from the isotropic phase.

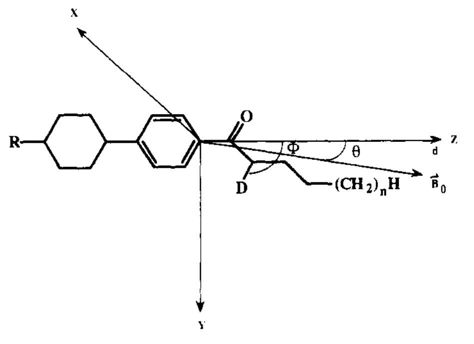

Figure 8. Vector representation of a C–D bond of **2** in the magnetic field (B_0); d is the director, θ is the angle between the magnetic field vector and the director axis, and Φ is the angle between the director axis and a C–D bond. R = C_7H_{15}; n = 3 for **2a** and n = 5 for **2b**.

ferred over the cis in all neat phases of **2** is attributed to the greater steric strain intrinsic to the cis isomer.

The E/C photoproduct ratios (Scheme I) are a sensitive measure of the ability of triplet hydroxy 1,4-biradicals (**BR**) to adopt rather well-defined pre-product conformations.[20] γ-H abstraction produces a conformation (**i-BR**) in which the p-orbitals on the radical centers are orthogonal. Conversion of **i-BR** into the cisoid biradical conformations leads to cyclization products (following intersystem crossing), while elimination products arise from transoid conformations. Although cisoid conformers may also give rise to elimination products, their mode of reaction when derived from molecules like **2** (which do not possess intramolecular strain and are not sterically encumbered at the reaction center) appears to be predominantly cyclization.[21] Formation of cyclization products requires significant overlap of the singly occupied p-orbitals on the radical centers.[20] To fulfill this requirement, rotation of the bulky aryl substituent on the hydroxyl-substituted radical center of **i-BR** must occur. Such motions, and the resulting cisoid conformations, are especially taxing on ordered environments

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(20) For reviews of Norrish II photoreactions, see: (a) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168. (b) Wagner, P. J. In *Rearrangements in the Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3. (c) Wagner, P. J. *Acc. Chem. Res.* **1983**, *16*, 461. (d) Wagner, P. J.; Park, B.-S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1991; Vol. 11, Chapter 4.

(21) (a) Scheffer, J. R.; Trotter, J. *Rev. Chem. Intermed.* **1988**, *9*, 271. (b) Caldwell, R. A.; Dhawan, S. N.; Majima, J. *J. Am. Chem. Soc.* **1984**, *106*, 6454.

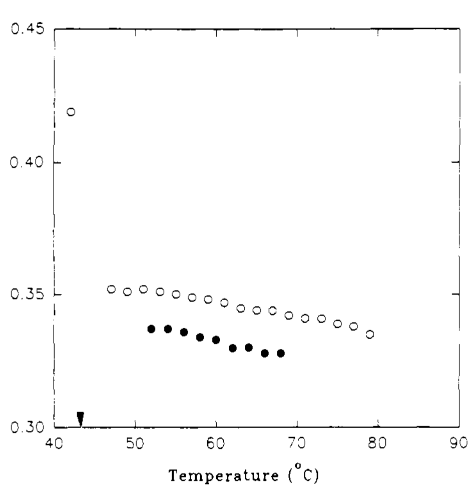

Figure 9. Variation of the order parameter, S_{zz}, with temperature (°C) in the smectic B phase of **2a** (○) and **2b** (●). The arrow indicates the smectic B to solid phase transition for **2b**.

with limited free volume. Formation of elimination products, on the other hand, requires overlap of the singly occupied p-orbital with the central C–C σ-bond being broken.[20] Such overlap is possible in the **t-BR** conformation whose nearly linear shape is more easily accommodated by a constrained matrix such as that of a liquid-crystalline or a solid phase. The motions required to interconvert i-**BR** into the trans conformer are essentially those necessary to form **c-BR** with an additional 180° rotation of the alkyl chain. It has been proposed that in ordered environments formation of **t-BR** from i-**BR** may occur by the motion of the alkyl chain alone, without involving the rotation of the aryl substituent on the hydroxy-substituted radical center.[22]

The triplet lifetimes of biradicals from alkylphenones in hydrocarbon solvents are about 70–80 ns.[23] During such a period, equilibrium among the various triplet biradical conformations is likely to be reached in the isotropic phases, perhaps in the smectic phases, but probably not in the solid phases. A triplet hydroxy 1,4-biradical must first undergo intersystem crossing to the singlet state which then gives rise to the photoproducts. Since singlet biradical lifetimes are extremely short[24] in comparison to the times required for conformational changes, no significant motional change is expected between the moment when the triplet biradicals undergo intersystem crossing and when the resultant singlets collapse to products. Thus, we associate the E/C product ratios directly with the relative amounts of transoid and cisoid biradicals present before intersystem crossing.[25]

Hydrogen bonding to the carbonyl group of a neighboring ketone may restrict the ability of a hydroxy 1,4-biradical to undergo conformational changes. The existence of hydrogen bonding in the smectic B and solid phases of an analogous solvent system has been demonstrated.[4]

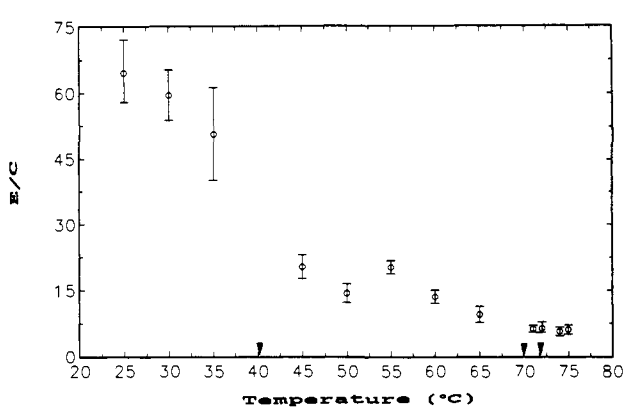

Figure 10. E/C product ratios from the irradiation of neat **2a** versus temperature (°C). Brackets show one standard deviation from the average. Arrows indicate phase transitions.

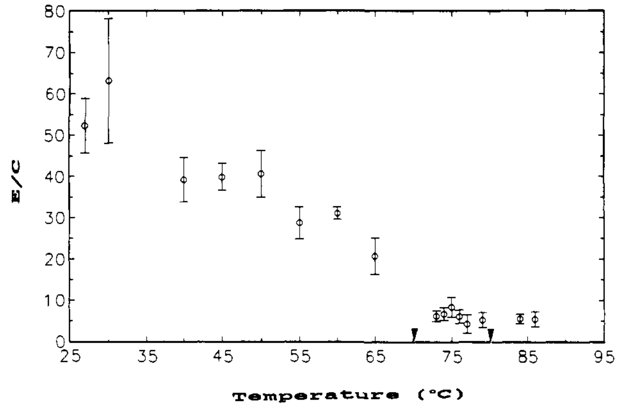

Figure 11. E/C product ratios from the irradiation of neat **2b** versus temperature (°C). Brackets show one standard deviation from the average. Arrows indicate phase transitions.

Plots of E/C ratios versus temperature for **2a** and **2b** are presented in Figures 10 and 11, respectively. In KI of **2a** and the solid phase of **2b**, significant product selectivity is observed. The E/C values in the solid phase of **2b** decrease with increasing temperature, perhaps due to the formation of additional defect sites and/or facilitated chain motion. The E/C ratios in KII of **2a** are considerably lower than those in KI, indicating that a larger free volume may be available to the reactive part of the ketone in its higher temperature solid phase. This result is consistent with the lower quadrupolar splittings obtained in KII for the deuterons on the methylene α to the carbonyl group. Product ratios comparable to those for **2a** were obtained upon irradiation of the two solid phases of **1**.[3]

From Figures 10 and 11, it is clear that there is no Norrish II product selectivity from the smectic B phases of **2**. Although both smectic phases exist over wide temperature ranges (with a large monotropic component), irradiation at monotropic temperatures resulted in E/C ratios which were indistinguishable from those of the solid phases. Apparently, the initially formed photoproducts which do not fit well in the monotropic phase lattice are able to accelerate the transition to the thermodynamically more stable solid phase. Strong evidence for this assertion is found in non-selective E/C ratios from irradiation of **2b** in the temperature range of its enantiotropic smectic phase.

Although solid phases of both **1** and **2** exhibit very large E/C ratios (ca. 50–75), they are less than the ratios measured upon irradiation of other ketones in solid matrices comprised of *foreign* host molecules.[4-6] Specifically, we cite the >100 E/C ratios from irradiation of 2-eicosanone in solid Phase I of heneicosane.[5] Thus, even in highly-ordered "homogenous" environments, such as those afforded by neat solid **1** or **2**, the loci of reaction may be somewhat more accommodating of **BR** motions than when in a matrix of different molecules; a larger free volume can be available conceivably in a neat crystalline matrix than when a molecule is made a part of a solid solution.

Additionally, a crystalline lattice does not preclude all motions; conformational changes of the type that would lead to **c-BR** and **t-BR** can occur in some systems. There are several reports of E/C ratios from Norrish II reactions in solid phases that are practically identical to those found in isotropic solutions of the same ketones.[26]

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(22) Hrovat, D. A.; Liu, J. H.; Turro, N. J.; Weiss, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7033.

(23) (a) Small, R. J., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1973**, *81*, 2126. (b) Wilson, R. M. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1985; Vol. 7, Chapter 5.

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(25) (a) Scaiano, J. C. *Tetrahedron* **1983**, *38*, 319. (b) Yang, N. C.; Elliot, S. P. *J. Am. Chem. Soc.* **1969**, *91*, 7750.

(26) See, for instance: (a) Ariel, S.; Ramamurthy, V.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1983**, *105*, 6990. (b) Scheffer, J. R.; Trotter, J.; Nalamasu, O.; Evans, S. V.; Ariel, S. *Mol. Cryst. Liq. Cryst.* **1986**, *134*, 169.

The selectivity is, thus, a function of the free volume available in the reaction cavity of a **BR**, the shape and rigidity of the cavity, and the availability and disposition of hydrogen bond acceptors (i.e., carbonyl groups on neighboring molecules of **2** in our case) along the cavity walls.

Furthermore, the irradiation times needed to achieve equal percents of conversion are qualitatively similar in the isotropic and smectic B phases but considerably longer in the solid phases. Restrictions, like those mentioned above on the conformational lability of **BR** intermediates, must also hinder the bending motions in the solid phases which are necessary to bring a γ-hydrogen to within an abstractable distance of the carbonyl oxygen during the excited triplet lifetime of **2**.[26b,27]

Conclusions. From the lack of selectivity in the Norrish II photoproducts obtained in the smectic B phases of **2**, it is apparent that sufficient chain mobility and free volume exist to accommodate easily the shape changes which occur along the reaction coordinate leading from **i-BR** to the bulkiest Norrish II product, *cis*-cyclobutanol. We attribute this to the presence of the cyclohexyl group in **2** which forces large intermolecular separations within a smectic layer and, in turn, allows a great deal of motional freedom to the methylene groups near a layer boundary. In the solid phases of **2**, the mobility and free volume associated with the alkyl chain is reduced and, as a result, E/C ratios show high selectivities. The restrictions to motion in the solid state are probably exacerbated by hydrogen bonding of the hydroxyl groups of **BR** intermediates to carbonyl groups on neighboring ground-state ketone molecules.

Deuterium NMR spectroscopy in the smectic B phases of **2**, deuteriated at the carbon atom α to the carbonyl group, indicates that methylene groups near the central rings (and far from a layer boundary) exist in a motionally restricted environment. The proximity of the deuterons to the phenylcyclohexyl group allows them to sense the structural rigidity and greater order of the molecular core more than methylene groups near the end of the alkyl chains. This assertion is supported by results obtained by Boden et al., who observed that the quadrupolar splitting from deuterons on the alkyl chain of **8CB** in its smectic A phase decreases from 62 kHz to ca. 3 kHz upon moving from the methylene bound to the biphenyl core to the terminal methyl group.[18]

It should be remembered that our NMR experiments probe *ground state* motions of **2**, while the Norrish II product ratios depend upon the ability of **BR** intermediates to interconvert; the motions being sampled by the two experiments are not the same. As such, the two experimental probes complement each other only insofar as the motions are related. Clearly, the NMR experiments are pertinent to the ability of the triplet states of **2** to abstract a γ-hydrogen atom and form **i-BR**; subsequently motions associated with the eventual formation of products (Scheme I) are probably not related closely to the most common motions of **2** and should not be linked too closely to the ^{2}H NMR results. In a similar sense, the X-ray structural data relate to the conformations of **2** which are most stable, *but* not to the ability of **2** to deviate from those conformations and form shapes analogous to those shown in Scheme I.

In support of these assertions, ^{2}H NMR spectra of α-deuteriated **1** in its nematic phase show a large quadrupolar splitting (32–48 kHz) indicative of a well-ordered environment. However, no Norrish II photoproduct selectivity was observed upon irradiation of the ketones in their nematic phases. Likewise, no Norrish II photoproduct selectivity has been found from irradiation of guest ketones dissolved in several nematic solvents.[28,29]

Pronounced Norrish II selectivities have been observed from the irradiations of dopant ketones whose size and shape allow them to fit well in the smectic B phases of *n*-butyl stearate (**BS**) and **BCCN**.[4,22,28–32] In these cases, the probable mode of dissolution permits the locus of reaction of the guest ketone to lie within the more ordered region of the smectic layers of the host. Conversely, the selectivity from a group of isomeric ketones decreases markedly as the locus of reaction approaches a layer boundary of smectic **BS**.[4] This is the situation which obtains when smectic **2** is irradiated.

These results, taken in toto, demonstrate the necessity to maintain close packing among *groups* in neighboring molecules if the influence of solvent anisotropy is to be manifested in the rates or selectivities of the reacting species.

Experimental Section

Instrumentation. The equipment and protocols used for optical microscopy, DSC, analytical gas chromatography (GLC), and NMR have been described previously.[3] X-ray diffraction was carried out on a Scintag 2000 X-ray diffractometer using Cu Kα radiation (1.5406 Å) and 40 KV and 20 mA settings. Data analyses were performed on a Digital Microvax 2000 computer. The ketones (ca. 300 mg) were packed as powders into flattened copper sample plates and thermostated using a Lake Shore Cryotronics temperature controller (Model DRC91L) which had been calibrated with melting point standards.

Materials. The **2** were synthesized via a Grignard reaction of *trans*-4-heptyl(4-cyanophenyl)cyclohexane (Merck Licristal, ZLI-115, 99% pure) and 1-bromohexane for **2a** or 1-bromooctane for **2b** (both Aldrich reagents, 99%) according to the general procedure reported previously.[33] Both ketones were >99% pure after recrystallizations from ethanol, as determined by GLC.

***trans*-1-Heptyl-4-(4-heptanoylphenyl)cyclohexane (2a).** ^{1}H NMR (CDCl$_3$/TMS): δ 7.81 (2 H, d, J = 8.1 Hz, aromatic), 7.21 (2 H, d, J = 8.1 Hz, aromatic), 2.89 (2 H, t, methylene α to the carbonyl group), 2.45 (1 H, t, cyclohexyl proton α to the phenyl group), 1.81 (4 H, m, cyclohexyl), 1.66 (2 H, m, methylene β to the carbonyl group), 1.1–1.6 (21 H, cyclohexyl and methylenes), and 0.8–1.1 ppm (8–9 H, methylenes and methyl). UV (hexane): λ_{max} 206 (ϵ_{max} 1.5×10^4 M^{-1} cm^{-1}), 252 (ϵ_{max} 1.3×10^4 M^{-1} cm^{-1}), and 322 nm (ϵ_{max} 68 M^{-1} cm^{-1}).

***trans*-1-Heptyl-4-(4-nonanoylphenyl)cyclohexane (2b).** ^{1}H NMR (CDCl$_3$/TMS): δ 7.81 (2 H, d, J = 8.1 Hz, aromatic), 7.21 (2 H, d, J = 8.1 Hz, aromatic), 2.90 (2 H, t, methylene α to the carbonyl group), 2.50 (1 H, m, cyclohexyl proton α to the phenyl group), 1.88 (4 H, m, cyclohexyl), 1.69 (2 H, m, methylene β to the carbonyl group), 1.1–1.5 (25 H, cyclohexyl, methylenes, and methyl), and 0.84 ppm (3 H, m, methyl). ^{13}C NMR (CDCl$_3$): δ 200 (carbonyl), 153, 135, 128, 127, 44.8, 38.6, 37.3, 34.0, 33.4, 31.9, 30.0, 29.4, 29.1, 27.0, 24.5, 22.7, and 14.1 ppm. UV (hexane): λ_{max} 206 (ϵ_{max} 1.8×10^4 M^{-1} cm^{-1}), 252 (ϵ_{max} 1.9×10^4 M^{-1} cm^{-1}), and 322 nm (ϵ_{max} 75 M^{-1} cm^{-1}).

The elimination product (**3**) from irradiation of **2** was identified by GLC co-injection with authentic materials whose syntheses and characterization have been previously reported.[3] The cyclization products **4** were identified by their GLC behavior as compared to that of the separated and characterized cyclization products of **1**.[3]

Deuteriation of **2** at the methylene carbon α to the carbonyl group was accomplished by treatment with deuterium oxide (MSD Isotopes, 99% *d*) and Na$_2$CO$_3$ in monoglyme (Aldrich, anhyd, 99%).[34] Deuterium exchange >90% at the α methylene was established by comparison of the ^{1}H integrals at 2.9 ppm of treated and untreated **2**.

Irradiation Procedure. Sample preparation, irradiation, and analysis procedures have been described previously.[3]

Acknowledgment. We thank Prof. Geoffrey B. Jameson for valuable discussions in analyzing the X-ray data and E. Merck for its generous donation of the Licristal ZLI-115. R.G.W. gratefully acknowledges the National Science Foundation for its support of this research.

Registry No. 2a, 141784-31-8; **2b**, 141784-32-9; *trans*-4-heptyl-1-(4-cyanophenyl)cyclohexane, 61204-03-3; 1-bromohexane, 111-25-1; 1-bromooctane, 111-83-1.

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