photochemical processes occur from the excited singlet state.

Fischer et al.[3] have reported that, upon cooling N4PH, the tautomeric equilibrium shifts toward the hydrazone form of N4PH in methylcyclohexane or toward the azo form in methanol. The alcoholic solution of −140 °C contains practically only the trans azo form, which showed a strong absorption band with a maximum at $\sim$410 nm. Upon steady-state irradiation at 546, 365, 436, and 405 nm in ethanol, the trans azo form was found[3] to be photoequilibrated with its cis isomer which showed weak absorption maxima at $\sim$340 and $\sim$480 nm. In turn, the unstable cis isomer was thermally converted into the trans isomer via the phenylhydrazone. We have carried out a study of this same compound using laser flash spectroscopy techniques. First, we looked at the azo form in ethanol at −75 °C. This was done to compare the quality of agreement between our results using laser flash techniques with those of Fischer[3] who employed steady-state techniques. We also wanted to determine if transients could exist and be isolated at such temperature. We have reported that laser flash irradiation at 355 nm of N4PH in ethanol at −75 °C gave two bands of absorption with maxima at 340 ± 10 nm and 480 ± 10 nm. These results are the same as those seen before[3] when the trans azo was converted to the cis isomer by steady-state irradiation.

We have reported that flash irradiation at 355 nm of the hydrazone form of N4PH in methylcyclohexane at −75 °C (where the absorption maximum is at 483 nm) gave a product with a maximum positive ΔOD at 410 ± 10 nm which did not show any decay in the 0.5–400-μs time domain. Given the fact that no intramolecular proton transfer can occur and given the results we discussed earlier, we assign the spectral changes to be the result of the anti ↔ syn isomerization of N4PH in the hydrazone form. This isomerization is in marked contrast to what Fischer et al. have reported.[3] For them, no direct photoconversion involving the hydrazone form of N4PH seemed to take place.

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Norrish II Reactions of Neat Liquid-Crystalline Ketones. Comparison between Nematic and Solid Phase Order and Control of Photoproduct Distributions[1,2]

Inna Furman and Richard G. Weiss*

Contribution from the Department of Chemistry, Georgetown University, Washington, D.C. 20057.

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Abstract: The Norrish II photoreactions of *trans*-1-(4-pentanoylphenyl)-4-pentylcyclohexane (**1a**) and *trans*-1-heptyl-4-(4-pentanoylphenyl)cyclohexane (**1b**) have been examined in their solid, nematic, and isotropic phases. The influence of phase on the product distributions is found to be negligible in the nematic but significant in the solid phases. Phase order, probed by deuterium NMR spectroscopy of the compounds deuteriated at the methylene α to the carbonyl group and by differential scanning calorimetry, has been correlated with the photochemical results. The lack of influence of the nematic phase on the Norrish II reactions of neat **1** is consistent with previously reported results obtained from irradiations of ketones doped in inert nematic matrices. The influence of solid phase order on the photoproduct selectivity of **1** is greater than that observed in some studies on analogous guest ketones in other solid phase hosts, but smaller than in others. A discussion of some of the factors leading to phase control over molecular motions along a reaction coordinate is presented.

Introduction

Norrish II photoreactions of ketones (Scheme I) have been employed for several years to probe the steric and electronic microenvironments afforded by a variety of ordered media.[3] Among these are liquid crystals,[4-11] where the control over the probe reactions by various phases has ranged from being very high to undetectable. In the solid phases of the same media, the control by solvent has been usually, but not always, greater. When analyzing results in these studies, it has been necessary to consider the influence of the ketones on their cybotactic region (i.e., the whole volume in which the molecular order of the solvent has been affected by the solute[12]) in addition to the intrinsic order of the medium.

As a means to avoid complications from a solute's disturbance of its local environment and to compare directly the control that liquid-crystalline and solid phases exert over a ketone's photoproduct selectivity, we have examined the Norrish II reactions of two mesogenic ketones, *trans*-1-(4-pentanoylphenyl)-4-pentylcyclohexane (**1a**) and *trans*-1-heptyl-4-(4-pentanoylphenyl)cyclohexane (**1b**), in their neat isotropic, nematic, and solid phases. Monotropic smectic phases form but are too unstable to obtain reliable data. The photolyses are complemented with results from differential scanning calorimetry (DSC), ^{2}H NMR spectroscopy on **1a** and **1b** deuteriated at the methylene group α to the carbonyl, and optical microscopy. We have also reinvestigated and reassigned the phases of **1a** and **1b** based upon our observations.

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(1) Part 43 in our series Liquid-Crystalline Solvents as Mechanistic Probes. For Part 42, see: Sheikh-Ali, B. M.; Weiss, R. G. *Liq. Cryst.* **1991**, *10*, 575.

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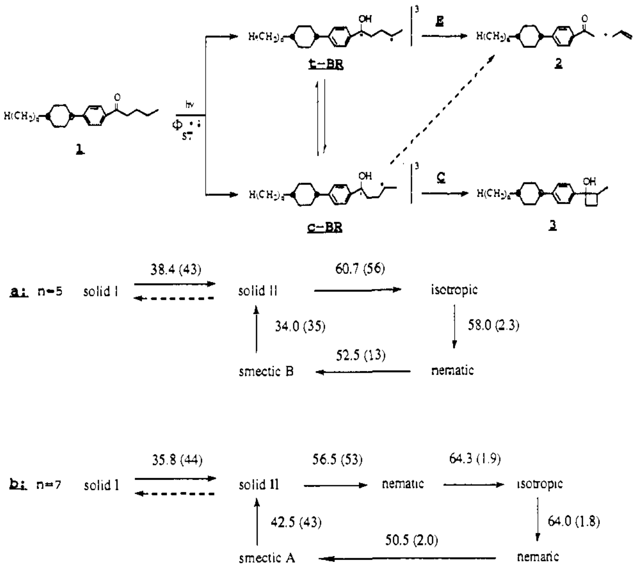
Scheme I Norrish II Reactions of **1a** and **1b** Showing t-BR and c-BR, the Biradical Precursors of Photoproducts **2** and **3**[a]



[a] Transition temperatures (°C) and heats of transitions (J/g) in parentheses from heating and cooling of **1a** and **1b** are included, also.

The overall conclusion reached in this study is that the "undisturbed" environment afforded by a neat phase and the "disturbed" environment provided by a foreign host may be equally selective (or the "disturbed" may be even *more* selective) with respect to the motions necessary to convert ketones like **1** to their photoproducts **2** and **3**.

Results and Discussion

Phase Behavior of 1. The syntheses and phase behavior of both **1a** and **1b** had been reported by Osman and Huyhn-ba.[13] Although we were able to use their synthetic procedure to produce molecules whose spectral properties fit the structure of **1a** and **1b**, the phase types and transition temperatures measured from optical microscopy and DSC did not correspond to the published values. The transition temperatures and phase types in Scheme I are from our data. A nematic phase has molecules arranged on average with their long molecular axes parallel to one another.[14] A smectic phase has molecules aggregated in layers which are stacked on top of each other.[14] In a smectic A phase, the long molecular axes are normal to the planes defined by the layers; in a smectic B phase, the molecules are aligned as in a smectic A phase, but with hexagonal arrangement within a layer.[14]

The monotropic smectic phases, especially, are very unstable. After being cooled from the isotropic phase to a smectic temperature, samples reverted to solid II after 10–30 min. The transformation from solid II to solid I was much slower. Presumably, pure solid I is isolated from recrystallizations of the ketones from ethanol. The degree of reversion from solid II (the higher temperature solid phase, KII) to solid I (the lower temperature solid phase, KI) after initial heating to the isotropic phase could be estimated by comparing the magnitude of the KII–KI enthalpy of transition in DSC thermograms of freshly crystallized and solid II-derived samples. DSC data indicate that **1a** reverts to the KI only partially after several days while the transition from KII to KI of **1b** is complete within several hours (Figure 1).

Below their enantiotropic temperature ranges, the monotropic nematic phases of **1** are relatively stable. They can be manipulated for several hours without apparent change. As a result, photochemical and spectroscopic results on **1** could be obtained throughout the supercooled nematic phase.

Phases were identified primarily by optical microscopy. Optical patterns of mesophases could be distorted by applying pressure to the cover slips sandwiching samples or by sliding one slip with respect to the other. The nematic phases exhibit a classic schlieren texture when viewed through cross-polars (Figure 2c).[15] The monotropic smectic phase of **1b** exhibits a fan-shaped texture characteristic of the smectic A phase while that of **1a** shows a mosaic pattern, indicative of a smectic B phase (Figure 2, d and f).[15]

The packing arrangements of the solid I and solid II phases are unknown. On the basis of the small enthalpy of transition between the smectic and solid II phases (Scheme I) and what is known about the solid phases of similar mesomorphic molecules,[5,16] we suggest that the solid II phases of **1a** and **1b** are layered, also, and perhaps partially interdigitated. The magnitude of the solid I–solid II enthalpy of transition and the fact that the transition can be detected easily by optical microscopy indicate that the two solid phases are packed very differently.

Deuterium Magnetic Resonance Studies. Insights into the structure of the various phases of **1** are provided by deuterium magnetic resonance spectroscopy of the α-deuteriated ketones. The magnitude of the quadrupolar splitting ($\Delta\nu$) obtained from this method provides information on the restriction that phase order imposes on the motion about the C–D bonds, as well as on the molecule as a whole.[17] The $\Delta\nu$ values in each phase of **1a** and **1b** versus temperature are shown in Figures 3 and 4, respectively. Representative spectra obtained in each phase are shown in Figure 5 for **1a** and in Figure 6 for **1b**. A quadrupolar splitting that is close to the rigid molecular limit of 127.5 kHz[18] is found in each solid I phase. The $\Delta\nu$ values from deuteriated **1** in their solid II phases are significantly lower than those obtained in solid I, indicating a lower degree of order and greater conformational freedom available to molecules in solid II phases.

The nematic phases of both compounds align rapidly in the spectrometer magnet: their spectra consist of a sharp doublet. The nematic phase of **1b** on cooling from the isotropic phase persists over a 15° range. As the temperature is lowered, the quadrupole splittings increase (Figure 4) due to a decrease in thermal motions. The quadrupolar splittings of **1b** can be used to calculate the order parameter, S_{zz},[19] which relates the average orientation of the C–D bonds to a defined axis system (Figure 7).

$$\Delta\nu = 3/2(e^2qQ/h)S_{zz} \qquad (1)$$

In eq 1, e^2qQ/h is the quadrupolar coupling constant (170 kHz for a deuterium atom bound to an aliphatic carbon atom[17b]), and it is assumed that both the quadrupolar interaction is axially symmetric and the z-axis is parallel to the molecular director[18] (Figure 7). Figure 8 depicts the variation of the order parameter with temperature in the nematic phase of **1b**. An analogous dependence of the order parameter on temperature was observed with nematic **1a** (Figure 1), but the narrow phase range (5.5°) made a systematic study difficult. The $\Delta\nu$ values and S_{zz} for nematic **1a** at 54.5 °C are 35.0 kHz and 0.137, respectively.

S_{zz} is assumed to be positive for **1** on the basis of spectral evidence obtained with a deuteriated homologue, *trans*-1-heptyl-4-(4-nonanoylphenyl)cyclohexane (**1c**), which exhibits positive magnetic anisotropy.[20] The smectic phase of α deuteriated **1c** yields a Pake pattern when heated from the solid to the smectic phase, and an aligned doublet when cooled to the smectic phase from the isotropic phase. Since $\Delta\nu_0$ of the Pake pattern corresponds to the splitting of the aligned doublet, the director of **1c**

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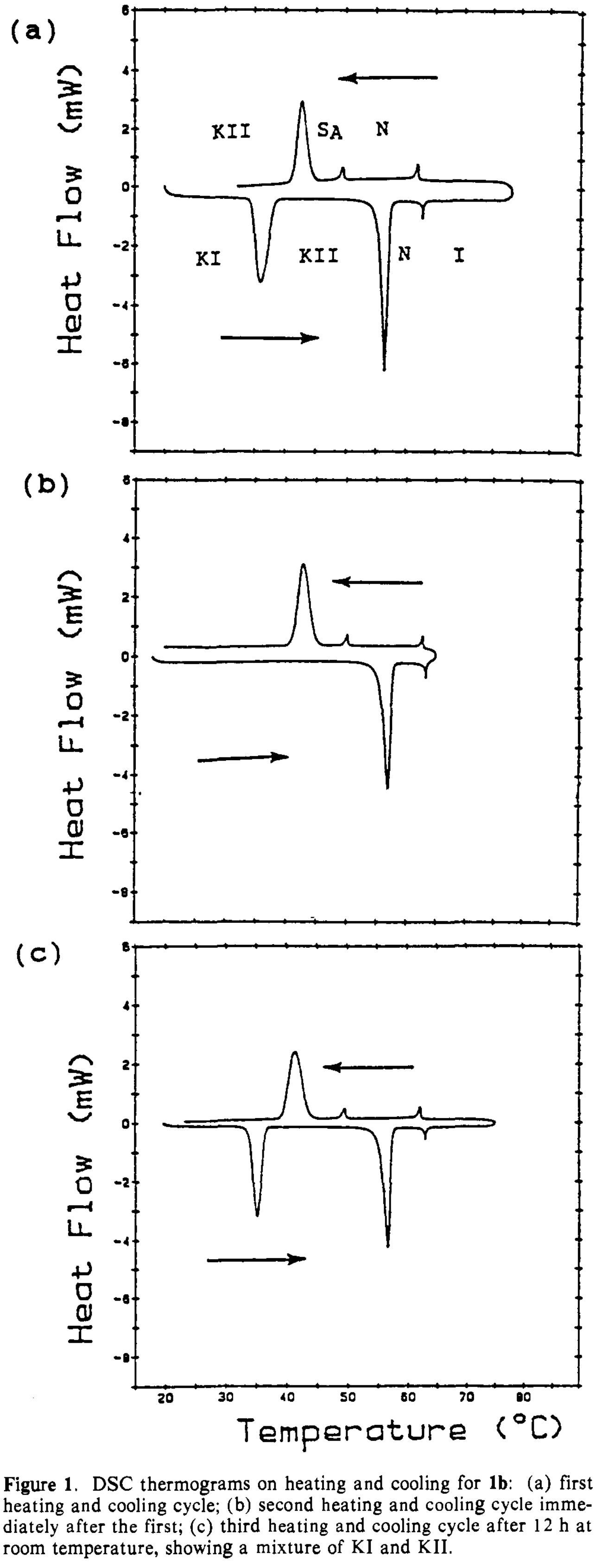

Figure 1. DSC thermograms on heating and cooling for **1b**: (a) first heating and cooling cycle; (b) second heating and cooling cycle immediately after the first; (c) third heating and cooling cycle after 12 h at room temperature, showing a mixture of KI and KII.

must be parallel to the applied magnetic field.

A monotropic smectic A phase of **1b** was detected upon cooling from the nematic phase. However, it crystallized to the solid II phase within 20 min at 51.5 °C. The sharp doublet obtained in the smectic phase indicates that the alignment induced in the nematic phase is retained by the smectic phase (see Figure 6f). The calculated S_{zz} value for smectic **1b**, 0.240, indicates that the restraints to C–D motions are greater than in the nematic phase and much less than expected in the solid phases.

For molecules with structures related to **1**, the quadrupolar splittings of deuterium atoms on an alkyl chain have been reported;[21] the S_{zz} calculated according to eq 1 are comparable to the values found for **1**. For example, the $\Delta\nu$ of the methylene group β to the biphenyl of 4-*n*-octyl-4′-cyanobiphenyl (**8CB**) was reported in the nematic phase (33 °C) to be 32 kHz,[21] corresponding to an order parameter of 0.125. In the smectic phase (27 °C), S_{zz} is approximately 0.24 ($\Delta\nu$ ca. 60 kHz[21]).

Irradiations of 1 and Norrish II Photoproduct Ratios. The incident radiation was carefully filtered to minimize photoreactions occurring at the glass–ketone interface and to ensure approximately equal probabilities of excitation throughout the neat samples. Thus, the neat ketones were irradiated at wavelengths where the optical densities and ketone extinction coefficients are small; Pyrex and a Corning 0-51 cut-off filter were found satisfactory for this purpose (Figure 9).

The mechanism of the Norrish II photoreactions of aromatic ketones like **1** (Scheme I) is fairly well understood and has been discussed in detail elsewhere.[22] The γ-H abstraction proceeds from triplet n,π^* states, producing long-lived triplet hydroxy-1,4-biradicals (70–80 ns for intermediates from alkylphenones in hydrocarbon solvents).[23] Due to orbital overlap considerations, two families of 1,4-biradical conformers are expected to be important precursors to products: elimination products arise from transoid biradicals; cyclization products must result from cyclization of cisoid conformers which may, in principle, also cleave to yield elimination products. Cisoid biradicals for ketones like **1**, which are relatively free of intramolecular strain at the locus of reaction, have been shown to give cyclization products almost exclusively.[5,24] On the basis of steric considerations, a cisoid 1,4-biradical should be more energetic than its transoid conformer. The greater yield of elimination products from irradiations conducted in isotropic phases supports this hypothesis.

Triplet 1,4-biradicals must undergo intersystem crossing before collapsing to products. Due to the very short lifetimes expected of the singlet biradicals,[25] there should be very little conformational change between the moment of intersystem crossing and the collapse of the singlets to products.[26] Thus, the E/C product ratios from irradiations in viscous media like the liquid-crystalline and solid phases of **1** should reflect the populations of the cisoid and transoid biradicals prior to intersystem crossing. Given their relatively long triplet lifetimes, triplet biradicals from **1** can probably achieve conformational equilibrium in their neat isotropic and nematic phases, but probably not in the solid phases.

It has been demonstrated that hydrogen bonding interactions between the hydroxyl portion of a biradical from a dopant ketone and the carboxyl group of a neighboring solvent molecule in ordered media can mediate the course of Norrish II reactions.[10] Such interactions are well-documented in isotropic media.[22] They should also be quite important when the hydrogen bond acceptor is a carbonyl group from **1**. The influence of this hydrogen bonding may be more pronounced in the solid phases than in the isotropic and nematic phases if it is supported by the unit cell packing

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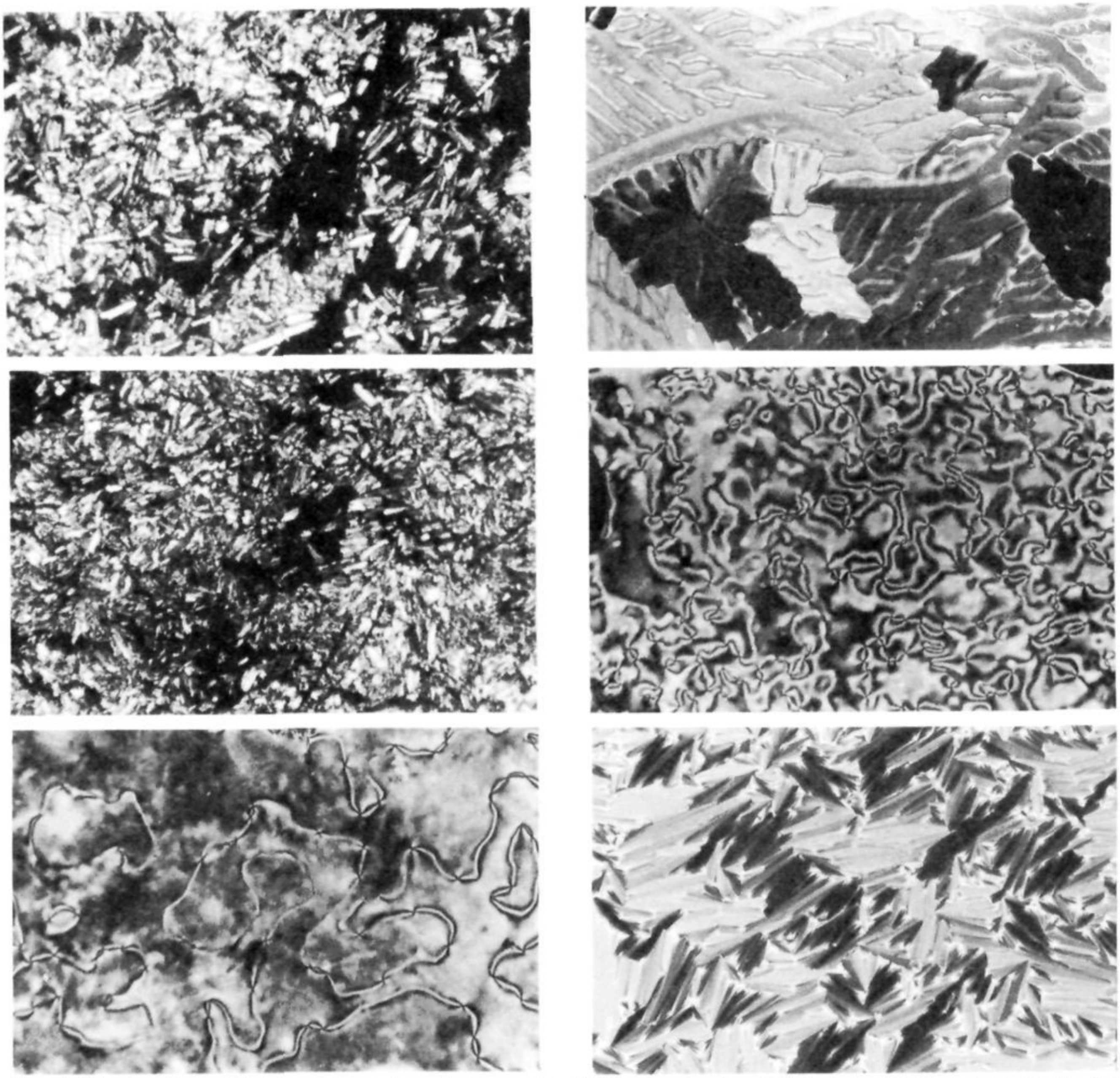

Figure 2. Textures of **1a** and **1b** as they appear under a microscope equipped with cross-polars (magnification is ca. 480): (a, top left) KI of **1a**, 30.0 °C; (b, middle left) KII of **1a**, 38.5 °C; (c, bottom left) the monotropic nematic phase of **1a**, 56.9 °C; (d, top right) the monotropic smectic B phase of **1a**, 51.6 °C; (e, middle right) the nematic phase of **1b**, 62.8 °C; (f, bottom right) the monotropic smectic A phase of **1b**, 48.2 °C.

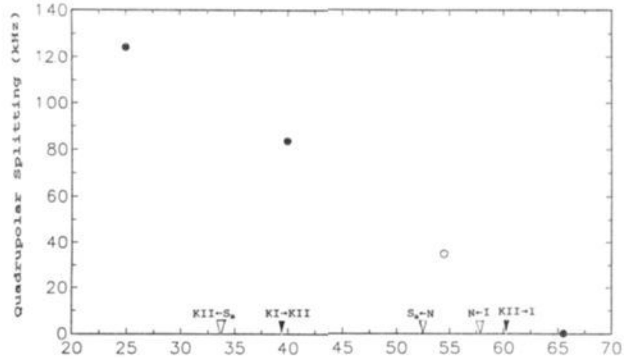

Figure 3. Plot of deuterium quadrupolar splittings (kHz) for **1a** versus temperature: heating from the solid I phase (●); cooling from the isotropic phase (○). Heating and cooling transitions are indicated with arrows.

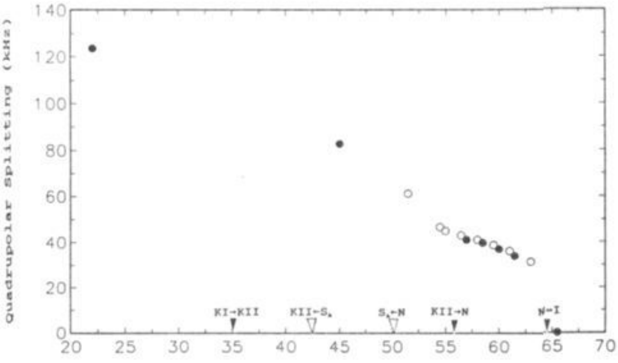

Figure 4. Plot of deuterium quadrupolar splittings (kHz) for **1b** versus temperature (°C): heating from the solid I phase (●); cooling from the isotropic phase (○). Heating and cooling transitions are marked with arrows.

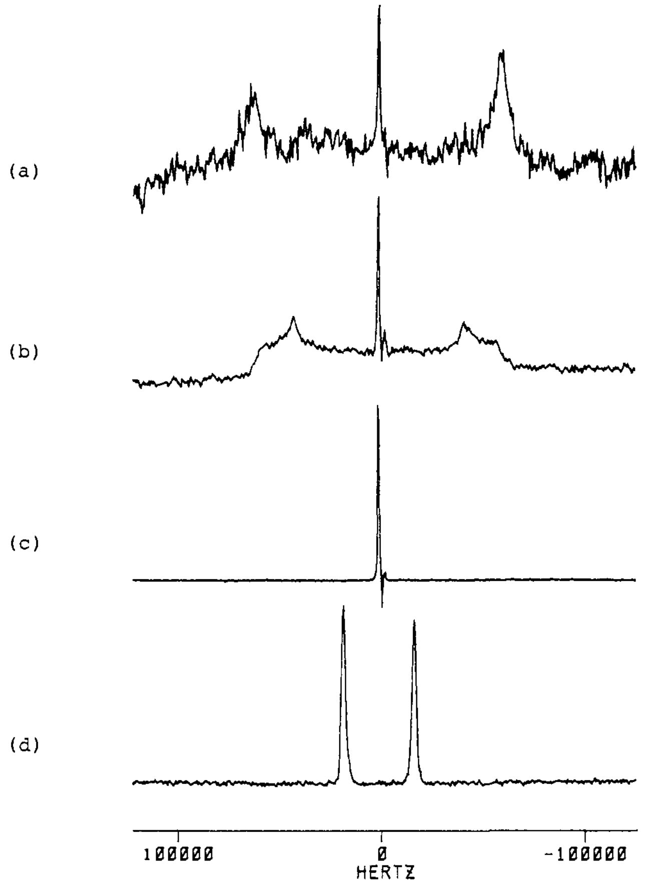

Figure 5. Deuterium NMR spectra of **1a**: (a) KI, 22 °C; (b) KII, 40 °C; (c) isotropic phase, 60 °C; (d) monotropic nematic phase, 54.5 °C upon cooling from the isotropic phase. The (a) and (b) spectra were obtained with a 10-s delay between scans and (c) and (d) with a 1-s delay.

arrangement. Since we have been unable, thus far, to grow single crystals suitable for X-ray diffraction studies, this point has not been explored experimentally.

For the most part, the effect of liquid-crystalline order on the course of the Norrish II reaction has been studied with ketones dissolved in mesogenic solvents.[4-11] Since a dopant ketone may perturb its local liquid-crystalline environment (as evidenced by depression of phase transition temperatures), the order of the neat host may not always be reflected in the photoproduct ratios of the guest molecule. In virtually all cases where liquid-crystalline order of the host has resulted in significant selectivity in E/C photoproduct ratios (i.e., a marked increase or decrease with respect to the isotropic value), the host and guest molecules have been similar in size and shape. Neat phases of ketones **1** provide systems free of solute disturbances and in which the conformational restraints that may be imposed on 1,4-biradicals in their nematic and solid phases should be more easily definable.

The photoproducts from **1** are mainly those from the Norrish II process. Minor side reactions are evident from analytical gas chromatography of irradiated samples, but with the low percent conversions used (<10%), these correspond to <1% of total products. Both diastereomeric cyclization products (*cis*- and *trans*-**3**) are formed from irradiation of **1** as evidenced by the isolation of both isomers from a preparative scale irradiation in benzene (see Experimental Section). However, only one peak attributable to the cyclization products was observed upon analyses of irradiated samples with several gas chromatographic columns. Thus, although both diastereomers of **3** are being formed upon irradiation of **1**, their ratios could not be measured routinely.

E/C product ratios from irradiation of **1b** versus temperature (and phase type) are shown in Figure 10. The nearly temperature independent product ratios obtained from irradiations in benzene are also included. The ratios from irradiation of **1b** in its solid II phase increase steadily with decreasing temperature and then become constant in the solid I phase. Increasing temperature in the solid II phase may cause additional defect sites to form and/or facilitate simple chain motions. The lower E/C ratios from irradiation in solid II than in solid I suggest that a larger free volume may be available intrinsically to the ketones in the higher temperature phase in addition to the greater thermal motions from kT.

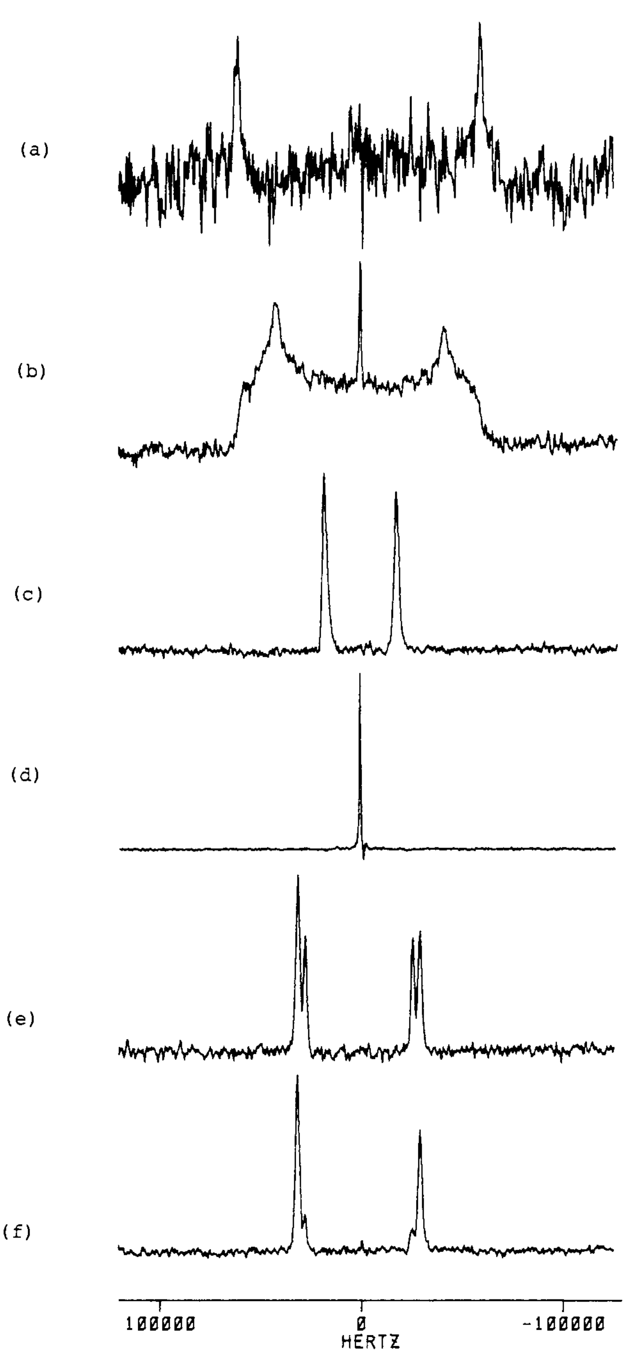

Figure 6. Deuterium NMR spectra of **1b**: (a) KI, 22 °C; (b) KII on heating from KI, 45 °C; (c) nematic phase on heating from KI, 37 °C; (d) isotropic phase, 65.5 °C; (e) a mixture of nematic and monotropic smectic phases on cooling from the isotropic phase, 51.5 °C; (f) as in (e) after 10 min. The (a) and (b) spectra were obtained using a 10-s delay between scans and (c)–(e) with a 1-s delay.

The E/C product ratios from **1a** versus temperature are shown in Figure 11. Product ratios on heating from the solid and on cooling from the isotropic phase were obtained. Since the monotropic smectic phase is not stable, the data in the 50–34 °C temperature range are assigned to reactions occurring in the solid II phase; similar photoproduct ratios were obtained at these temperatures from the irradiation of samples with and without

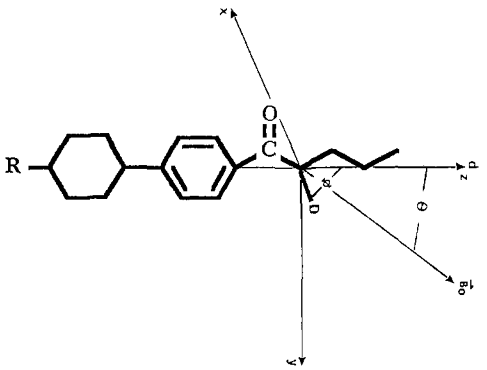

Figure 7. Vector representation of a C–D bond of **1** in the magnetic field (B_0); *d* is the director, Θ is the angle between the magnetic field and the director axis, and Φ is the angle between the director axis and a C–D bond.

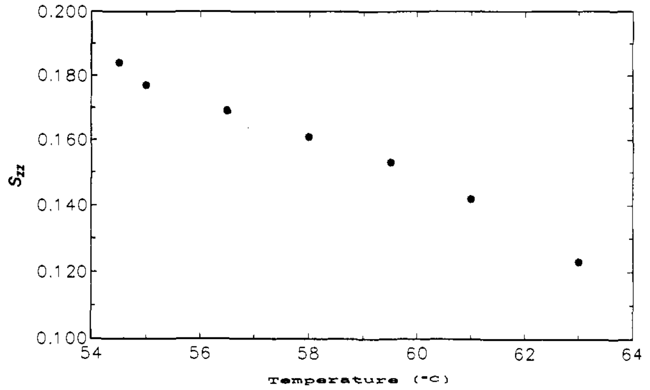

Figure 8. Plot of the variation of the order parameter, S_{zz}, with temperature (°C) in the nematic phase of **1b** on cooling from the isotropic phase.

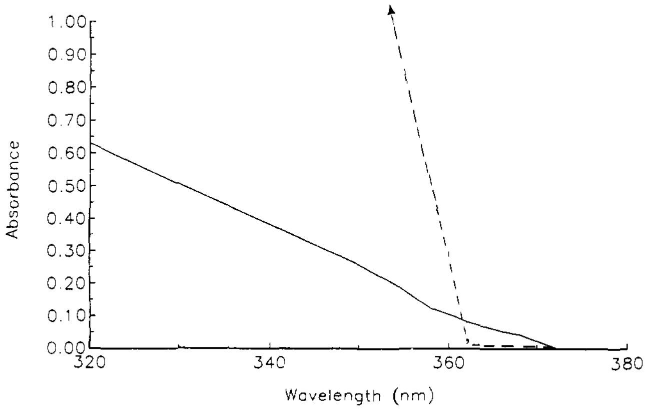

Figure 9. Plot of the absorbance spectra of 7.93 × 10^{-3} M **1b** in hexane (—) and our Corning 0-51 filter (---).

prior heating to the isotropic phase. The low E/C ratios for **1a** below 34 °C, compared to the solid I phase of **1b**, may be attributed to the lengths of time required for the two ketones to undergo the KII–KI phase transition. After initial heating to the isotropic phase, the KII–KI phase transition for **1b** occurs within a few hours while several days are required for **1a**. Hence, the data in Figure 11 below 34 °C arise from a mixture of solid phases.

Since our standard degassing procedure requires sample heating to the isotropic phase and, therefore, the unavoidable ambiguity between solid phases I and II, a different protocol was employed in several experiments. Samples were packed as solids from ethanol recrystallizations into capillary tubes and irradiated without heating. Resulting product ratios, shown in the insert of Figure 11, are of the same order of magnitude as those observed from irradiation of the solid I phase of **1b**. The irradiation times needed to achieve the same percent conversion using the above procedure for **1a** and in the solid I phase of **1b** are comparable and are significantly longer than those required in the solid II, nematic, and isotropic phases.

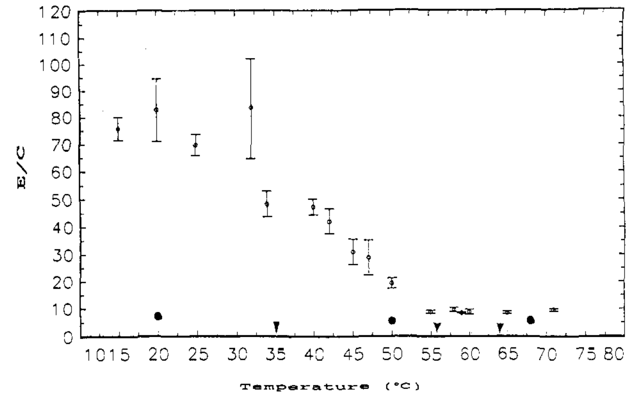

Figure 10. Plot of the E/C product ratios (○) from irradiation of neat **1b** versus temperature (°C), and (●) data from irradiations in dilute benzene solutions. Arrows indicate phase transitions (see Scheme I).

General Considerations. It is clear from Figures 10 and 11 that there is no meaningful difference between the E/C values from irradiation of **1** in the nematic and isotropic phases. However, the magnitudes of the deuterium quadrupolar splittings of deuteriated **1** in its nematic phase (32–48 kHz) demonstrate that the methylenes near the carbonyl group exist in a well-ordered environment; a singlet, indicative of rapid, uncorrelated motion, was the dominant feature only in the isotropic phase spectra.

The difference between the photolysis and the ^{2}H NMR data can be reconciled since they probe somewhat different motions. The deuterium magnetic resonance experiments sample the ground-state motions of the methylenes of the alkyl chain α to the carbonyl group, and the photolysis results are dependent on very specific motions of the entire alkyl chain and, perhaps, the phenyl group. In an ordered environment, like that provided by a neat liquid-crystalline phase, only a few conformations of an alkyl chain are expected to contribute significantly to the overall population. However, conformations of somewhat higher energy (like those responsible for γ-hydrogen abstraction and formation of the cisoid biradicals) may be important mechanistically.

Boden et al.,[21] studying the deuterium NMR spectra of nematic phase **8CB**, per-deuteriated along the alkyl chain, found that the quadrupolar splittings for the methylenes along the alkyl chain varied from ca. 35 kHz for the group α to the biphenyl to ca. 1.3 kHz for the terminal methyl. They also observed that the Δν of the terminal methyl group is larger in the less-ordered nematic phase than in the smectic phase. The Δν of all other methylene groups along the alkyl chain of **8CB** were larger in the smectic phase than in the nematic; this is the trend observed for α deuterons of **1b** (Figure 4). Thus, the order parameter, S_{zz}, reflective of the total molecular order (associated with intermolecular packing arrangements) and that associated with internal and external packing constraints of specific groups within a molecule must be considered as only somewhat related. It can then be concluded from the E/C product ratios and the ^{2}H NMR data from nematic phase **1** that the α methylenes are well ordered, on average, but that the 1,4-biradicals derived from **1** (and imbedded in their matrix) do not experience sufficiently greater restraints than in the isotropic phases to affect perceptibly their conformational preferences along the alkyl chain.

The inability of the nematic phase order of *trans,trans*-4′-alkyl[1,1′-bicyclohexyl]-4-carbonitrile (**BCCN**) to influence the course of the Norrish II pathways of aromatic ketones has also been reported. The temperature profile of the Norrish II reaction of a variety of ketones in **BCCN** was reported by Zimmermann et al.[5] Although quadrupolar splittings of 16–22 kHz[27] were measured for the α methylene groups of the ketones in nematic

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[27] Treanor, R. L.; Weiss, R. G. *J. Phys. Chem.* **1987**, *91*, 5552.

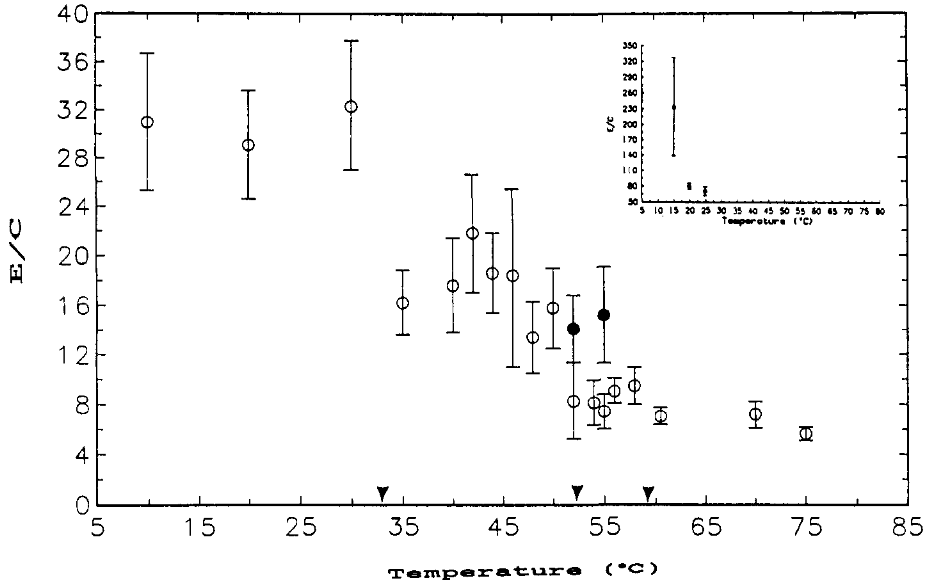

Figure 11. Plot of the E/C product ratios from irradiation of neat **1a** versus temperature (°C) on cooling from the isotropic phase (○) and on heating from the solid I phase (●). Arrows indicate phase transitions on cooling from the isotropic phase (see Scheme I).

BCCN, no photoproduct selectivity could be discerned. Workentin et al.[11] observed no difference in the photoproduct ratios from valerophenone, butyrophenone, or hexanophenone measured in the nematic and isotropic phases of **BCCN**. That the nature of the environment experienced by the three ketones in nematic **BCCN** is similar to that of **1** in their nematic phases is evidenced by the quadrupolar splittings observed for their α-deuteriated compounds. The $\Delta\nu$ values for the α-deuterium atoms on the three alkanophenones dissolved in the nematic phase of **BCCN** are 20–23 kHz, approximately one-half of the quadrupolar splittings found for neat nematic **1**. However, **BCCN** aligns its director perpendicular to an applied magnetic field[28] ($\theta = 90°$) while **1** aligns its director parallel to it ($\theta = 0°$). Since $\Delta\nu$ is proportional to S_{zz} (eq 1), the order parameters of the alkanophenone in **BCCN** are very similar (as measured by deuterium atoms on the carbons α to the carbonyl group). Also the $\Delta\nu$ of α-deuteriated butyrophenone in smectic **BCCN** is 32 kHz,[11] about one-half of the 61.3 kHz measured for **1b** in its smectic phase. If the directors of the molecules in the smectic phases retain their nematic phase orientations with respect to an external magnetic field, the order parameter of the alkanophenones in smectic **BCCN** and of smectic **1** are comparable as well.

Unlike the nematic phases, the solid II phases of both **1a** and **1b** led to significant selectivity in Norrish II product ratios. This result is consistent with the much larger quadrupolar splittings measured in the solid phases (Figures 3 and 4). However, the $\Delta\nu$ values are smaller than the rigid molecular limit, indicating that some freedom of motion for the alkyl chains remains in KII. The highest E/C ratios are expected and found from irradiations in the most ordered solid I phases. The photoproduct selectivity induced by the solid phases is assumed to be due to a combination of motional restraints imposed by the solid matrix and hydrogen bonding between the hydroxyl proton of a 1,4-biradical and the carbonyl group of a neighboring ketone. Matrix immobility may also be responsible for the slowness of the photoreactions in the solid I phase; significant barriers to adopting the geometry necessary for the initial γ hydrogen abstraction may be present. Similar arguments have been advanced by Slivinskas and Guillet to explain the photostability of 7-tridecanone in its solid phase.[29]

Our experiments do not allow bulk and defect site reactions to be differentiated. However, results from our irradiations of solid *sym*-alkanones indicate that defect site reactions of ketones like **1** should occur with very little selectivity.[6-9] The relatively large selectivities measured for the E/C ratios from **1** suggest that the vast majority of reacting molecules in the solid phases are located within the ordered bulk of the crystals.

Conclusions. Since E/C ratios from the photolysis of **1** in the solid I phases are ca. 75, cyclization is attenuated, but still possible. By comparison, Nunez and Weiss[9] found E/C ratios $\gg$ 100 from irradiation of 2-nonadecanone in the solid layered phase of eicosane and from 2-eicosanone in the lower temperature solid phase of heneicosane. He and Weiss[10] reported E/C ratios >100 for *p*-*n*-butylnonadecanophenone in the layered solid phases of *n*-butyl stearate. In other studies, lower E/C ratios than those observed for **1** in its neat solid I phase have been obtained from irradiation of ketones in the solid phases of their hosts.

Thus, a spectrum of photoproduct selectivities has been observed from irradiation of ketones in several layered solid phases. The ordering imposed on the reaction coordinate which converts **1** to its photoproducts in a solid matrix comprised of like molecules is *not* exceptional. The E/C ratios obtained from this system indicate that less or more ordered environments for the loci of Norrish II transformations in aromatic ketones can be afforded by solid matrices comprised of molecules which differ from the reacting species. This unanticipated result leads us to conclude that the amount and shape of the free volume near the locus of reaction in ketones undergoing Norrish II reactions in neat solid matrices (and, perhaps, the availability of receptors in neighboring molecules for hydrogen bonding with the intermediate 1,4-biradicals) are the most important factors controlling photoproduct selectivity. A neat solid matrix, per se, is insufficient to ensure high photoproduct selectivity.

Experimental Section

Instrumentation. NMR spectra were recorded on a Bruker AM-300 WB spectrometer equipped with an Aspect 3000 computer. A 5 mm H/C probe was used for ^1H and ^{13}C spectra with either $CDCl_3$ (MSD Isotopes, 99% *d*) or benzene-d_6 (MSD Isotopes, 99% *d*) as solvent and Me_4Si as reference. Deuterium spectra were obtained using a DuPont solids probe and an Amplifier Research 200L amplifier. Temperatures have been calibrated and are correct within ±2 °C. Melting points and phase transition temperatures were acquired on a Kofler hot-stage microscope equipped with crossed polars and are corrected. Photographs of the liquid-crystalline and solid phases of **1** were obtained on a Nikon Optiphot microscope equipped with a hot-stage, cross polars, and a Nikon FX-35WA camera. Total magnifications are indicated in Figure 2.

Differential scanning calorimetry curves were recorded with ca. 5-mg samples sealed in two-piece aluminum pans on a DuPont 1090 scanning calorimeter. The rate of temperature change was 2 °C/min. Analytical gas chromatography (GLPC) was performed using a Perkin-Elmer 4500 gas chromatograph (flame ionization detector) and an HP-17 (50%

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[29] Slivinskas, J. A.; Guillet, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 3043.

phenyl and 50% polysiloxane) 10 m × 0.53 mm wide bore column. UV spectra were recorded on either a Hewlett-Packard 8415A single-beam photodiode array or a Perkin-Elmer 452 double-beam spectrophotometer. Mass spectra were recorded on a Kratos MS-30 double-focusing dual-beam spectrometer at 20 eV ionizing voltage.

Materials. **1a** and **1b** were synthesized according to a previously reported procedure via a Grignard reaction starting with either *trans*-4-pentyl(4-cyanophenyl)cyclohexane (Merck Licristal/ZLI-114) for **1a** or *trans*-4-heptyl(4-cyanophenyl)cyclohexane (Merck Licristal/ZLI-115) for **1b** and 1-bromobutane (Aldrich, 99%). Both ketones were more than 99% pure as determined by GLPC after recrystallizations from ethanol.

trans- and *cis*-**3a** and **2a** were obtained from a solution of 300 mg of **1a** in benzene (Baker reagent) that had been purged with nitrogen for 5 min and irradiated to nearly 100% conversion. The photoproducts were separated on a silica (Baker, 60-200 mesh) column with 97/3 (v/v) hexane–ethyl acetate (Aldrich reagents) as mobile phase. *trans*-**3a** and **2a** were characterized by their ^{1}H and ^{13}C NMR spectra, mass spectra, and co-injection with irradiated samples of **1a** whose photoproduct retention times had been previously determined. *cis*-**3a** was identified by its proton NMR spectrum. Both diastereomeric cyclobutanols have characteristic cyclobutyl proton resonances in the 1.8–2.8-ppm region.[30] The ^{1}H spectrum of the trans isomer differs from that of the cis in the location of the doublet resonance corresponding to the protons of the methyl group on the cyclobutyl ring. For the cis isomer, the doublet resonated at 0.62 ppm (J = 6.9 Hz) while for the trans isomer it was found at 1.1 ppm (J = 6.9 Hz). The ^{13}C spectrum of the trans isomer showed a peak at 78.4 ppm characteristic of tertiary carbons bearing a hydroxyl group and its mass spectrum exhibited an m/e peak at 314, as well as M − 18 and M − 28 peaks characteristic of 1-phenylcyclobutanols.[30] On the silica chromatographic column, the cis isomer eluted after the trans.

2a has a melting point of 62.0–65.0 °C. NMR spectrum: 7.88 (d, J = 8.25 Hz, 2 H, aromatic), 7.25 (d, 8.25 Hz, 2 H, aromatic), 2.58 (s, 3 H, methyl α to carbonyl), 2.56 (m, 1 H, cyclohexyl α to phenyl group), 1.89 (d, 4–5 H, cyclohexyl), 1.2–1.1 (m, alkyl and cyclohexyl), 0.9 (t, 3 H, terminal methyl). The mass spectrum of **2a** exhibits an m/e peat at 272, its expected molecular ion.

2b was synthesized according to the same procedure used to obtain **1**, except methyl iodide (Fisher reagent) instead of 1-bromobutane was employed to form the Grignard reagent. **2b** exhibited mp 62.8–64.8 °C and a proton NMR spectrum almost identical to that of **2a**. The mass spectrum of **2b** displayed an m/e peak at 300, its expected molecular ion.

Treatment of either homologue of **1** with deuterium oxide (MSD Isotopes, 99% d) and Na_2CO_3 in monoglyme[31] (Aldrich, anhydrous, 99%) yielded ketone with >90% deuterium at the position α to the carbonyl group as determined from comparisons of the ^{1}H integrals of the α methylene resonances (2.9 ppm) from treated and untreated **1**.

Irradiation Procedures. Irradiations were performed with a Hanovia 450 W medium pressure Hg arc lamp. Temperature control was achieved using either a Haake HK-2 or a Forma Scientific circulating water bath. Prior to photolysis, samples were purged with nitrogen for ca. 5 min in their isotropic phases, transferred to (0.8–1.1) × 100 mm capillary tubes, and flame-sealed. Irradiations were performed through water, a Pyrex glass filter, and a Corning 0-51 cutoff (>30% at 380 nm) filter. Irradiations of three samples at each temperature were conducted to less than 10% ketone conversion. The contents of the capillaries were then dissolved in hexane (Aldrich, HPLC grade) and analyzed by gas chromatography. The E/C ratios, uncorrected for detector response, represent an average of triplicate analyses of each of the three samples at each temperature.

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Mixed-Valence, Conjugated Quinone and Imide Anion Radicals. An ESR Investigation

Stanton F. Rak and Larry L. Miller*

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received August 8, 1991. Revised Manuscript Received October 11, 1991*

Abstract: Anion radicals of linear polyacene diquinones and diimides were produced electrochemically and studied by ESR. The odd electron of substituted 1,4,8,11-pentacenetetrone anion radicals is localized (in a naphthoquinoid unit) and hops from one quinone to the other. The hopping rate was measured. The anion radicals of similarly sized anthracenetetracarboxylic acid 2,3:6,7-diimides have a delocalized odd electron, and there is relatively high electron density on the bridge. The results are compared to other unconjugated two-electrophore anion radicals.

Recent studies in our laboratories have been directed toward the synthesis and properties of linear, rigid polyacene quinones and imides.[1-5] These molecules were designed to have long delocalization lengths and more than one quinone or imide electrophore. These structural features led us to examine the optical and electrical properties of the anion radicals, which displayed unusual properties, indeed, including near-infrared (near-IR) absorption bands at wavelengths as long as 2000 nm[1-3] and electrical conductivities as high as 1 S cm^{-1}.[4] It was proposed that a central structural issue was the delocalization or localization of the unpaired electron. Based on cyclic voltammetry (CV), near-IR, IR, and ESR spectra, and molecular orbital (MO) calculations, anion radicals containing one aryl ring between the electrophore groups, e.g., $\mathbf{1}^-$ and $\mathbf{4}^-$, were classified as delocalized.[1,2] Anion radicals having naphthalene or anthracene bridges connecting quinone electrophores, i.e., $\mathbf{2}^-$ and $\mathbf{3a}^-$, gave very different optical spectra, and based upon MO calculations, it was suggested that the unpaired electron in these anion radicals was localized on one quinone unit at any instant.[3] As such, the anion radicals could be considered mixed-valence species.

π-Electron localization was unexpected because the two electrophores of $\mathbf{2}^-$ and $\mathbf{3a}^-$ are formally part of a planar, conjugated π-system. In the present study ESR was used to examine this

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