

a nonbranching reaction sequence.³ Therefore, if we consider the first bond cleavage reaction to be irreversible for both the indole- and quinone-sensitized cleavage reactions, we would predict all of the isotope effect to be associated with cleavage of the 5,5 bond in the indole case and with cleavage of the 6,6 bond in the quinone case. Observation of an isotope effect associated with cleavage of the second bond in each case would be indicative of one or more of the following: (a) a β -secondary isotope effect associated with the first bond cleavage, (b) reversible first bond cleavage, and (c) concerted cleavage of both bonds.

On the basis of previous mechanistic studies on the fragmentation of the photodimer radical cation, we propose that the isotope effects measured for the anthraquinone-sensitized cleavage support a stepwise mechanism where the first bond cleavage is effectively irreversible.^{7,11-14} The small effect on the 5,5 bond cleavage may thus be due to a hyperconjugative effect¹⁵ or due to the small hybridization change occurring at C5 due to elongation of the 6,6 bond in the transition state.¹⁶

For the radical anion fragmentation, the relatively large isotope effect observed with the 6,6-dideuterio photodimer may be indicative of an intrinsically different transition state for the first bond cleavage of the radical anion compared to the radical cation leading to a larger secondary β -isotope effect. Alternatively, since the fragmentation of the photodimer radical anion is estimated to be $\sim 10^3$ times slower than the radical cation fragmentation,¹⁷ the large 6,6 isotope effect may be due to reversibility of the 5,5 bond cleavage. Thirdly, the pattern of effects observed for the indole-sensitized cleavage is also consistent with a concerted fragmentation with an asymmetric transition state.

The previously published isotope effect studies on the DNA photolyase catalyzed cleavage of deoxyuridine dinucleotide photodimers are shown in Table III.⁴ While these isotope effects are clearly not identical to either of the model systems due to the different forward commitment factors for the models and the enzyme, the pattern (i.e., substantial isotope effects for both the cleavage of the 5,5 and the 6,6 bonds) is similar to that observed for the indole-sensitized cleavage. Thus, we propose that the enzymatic reaction proceeds via the fragmentation of a photodimer radical anion. Studies utilizing photodimers substituted with an iodomethyl radical trap¹² are now in progress to examine the timing of the bond cleavage steps.

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Registry No. 1, 138572-10-8; 5, 138572-11-9; DNA photolyase, 37290-70-3; deuterium, 7782-39-0.

Supplementary Material Available: Synthetic scheme for the preparation of the deuteriated photodimers (2 pages). Ordering information is given on any current masthead page.

(11) Previous studies on the reaction of the photodimer radical cation in related model systems have suggested that the fragmentation is a stepwise process^{7,12} and that it undergoes ring cleavage at a rate $\geq 10^9$ s⁻¹.¹³ Therefore the rate constant for the second bond cleavage has a lower limit of ca. 10^9 s⁻¹. Newcomb¹⁴ has recently measured the cyclization of the 2,2-dimethyl-5-cyano-4-pentenyl radical as proceeding with a rate of 1.9×10^4 s⁻¹. Hence, although reclosure of the one-bond-cleaved photodimer radical cation may be faster than the 2,2-dimethyl-5-cyano-4-pentenyl radical closure, it is unlikely that it will compete with the second bond cleavage.

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Tuning the Intermolecular Dative Interactions in Vanadium-Oxo Linear Chain Compounds: Formation of a New Type of Liquid Crystalline Polymer

Andre Serrette, Patrick J. Carroll, and Timothy M. Swager*

Department of Chemistry and
Laboratory for the Research on the Structure of Matter
University of Pennsylvania
Philadelphia, Pennsylvania 19104-6323

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Liquid crystals with transition-metal core groups (metallo-mesogens) are increasingly a topic of investigation since metals can impart useful shapes and properties which are not easily produced in totally organic liquid crystals.¹ A major distinction between metallomesogens and most organic mesogens is their greater tendency to exhibit intermolecular dative coordination in the solid state.¹ These interactions can result in phase behavior with kinetic, structural, and thermodynamic complexities, but they also provide an opportunity to create useful supermolecular organizations. We have been exploring the use of intermolecular dative coordination in liquid crystalline materials to create non-centrosymmetric assemblies with second-order nonlinear optical² and ferroelectric^{3,4} properties. Toward this end we have been investigating high oxidation state early metal monooxo complexes which have a propensity to exhibit either trigonal-pyramidal or square-pyramidal structures⁵ and in some cases assemble to give polymeric linear chain structures (e.g., $(-M=O \cdots M=O-)_n$) in the solid state. We have been focusing initially on the vanadyl Schiff-base complexes $n(\text{salen})\text{VO}$, $n(\text{salpn})\text{VO}$, and $n(\text{Me}_2\text{salpn})\text{VO}$ shown^{6,7} and report herein that $n(\text{Me}_2\text{salpn})\text{VO}$ species form a new type of unidirectional (head-to-tail) liquid crystalline linear chain polymer.

The $n(\text{salen})\text{VO}$ complexes are green polymorphic materials which all display smectic mesomorphic behavior. A high-tem-

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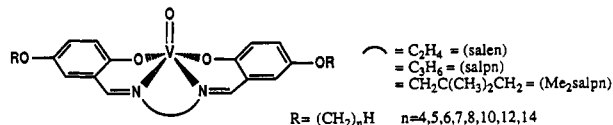
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perature smectic A (S_A) phase, identified by a homeotropic texture,⁸ is observed for $n = 10$ and 12, and one or two additional smectic phases with broken focal conic textures are present at lower temperatures for all of the compounds (Table I). X-ray diffraction of the low-temperature phases at 25 °C shows a single sharp peak at low angles and a broad amorphous halo at larger angles. For 8(salen)VO, the low-angle peak which corresponds to the interlayer spacing of 26.3 Å is considerably less than the molecule's length (34.9 Å), indicating that the smectic layers are tilted and/or highly interdigitated. The lack of intralayer positional order and our inability to produce a homeotropic texture lead us to the conclusion that the lower temperature phases (S_{C1}, S_{C2}, S_{C3}) are of the smectic C (S_C) variety.⁸ This data and a V=O stretching band at 973 cm⁻¹ (V=¹⁸O 934 cm⁻¹) which is insensitive to mesophase⁹ are both consistent with a monomeric structure for the n (salen)VO species.¹⁰

When propylene groups connect the Schiff-base nitrogens, orange n (salpn)VO complexes with a strong tendency toward linear chain formation result.¹¹ The n (salpn)VO's V=O stretching bands at 856 cm⁻¹ (V=¹⁸O 806 cm⁻¹), which are characteristic of linear chain formation,^{9,12} are 117 cm⁻¹ lower in energy than those of the n (salen)VO species. Unfortunately, the n (salpn)VO complexes do not exhibit liquid crystallinity, and they melt with decomposition at about 300 °C as shown in Table I.

Having determined that too rigid of linear chains can prevent liquid crystallinity, we investigated the n (Me₂salpn)VO species in which the steric interactions of the geminal dimethyls produce a slight weakening of the linear chain structure. This approach has been very successful, and all of the n (Me₂salpn)VO species are orange linear chain compounds with a V=O stretching band at 869 cm⁻¹ (V=¹⁸O 835 cm⁻¹), which is 13 cm⁻¹ higher in energy than the corresponding band for the n (salpn)VO species. An X-ray crystal structure performed on 7(Me₂salpn)VO confirms the linear chain structure (Figure 1) and shows that the molecules pack in a highly interdigitated layered structure. An elongation of the V=O in the linear chains relative to monomeric vanadyl complexes¹³ indicates that there are substantial intermolecular interactions and this organization is more than a crystal packing effect.

Differential scanning calorimetry of the n (Me₂salpn)VO species shows two major enantiotropic mesophases (Table I). Variable-temperature IR studies reveal the presence of linear chain structures in both of these liquid crystalline phases. Our results for 8(Me₂salpn)VO indicate that the linear chain structure disassembles above its isotropic point (171 °C), and the V=O band shifts to higher energy (987 cm⁻¹), as is characteristic of a monomeric complex.¹⁴ Cooling the complex into its higher tem-

Table I. Phase Behavior of n (salen)VO, n (salpn)VO, and n (Me₂salpn)VO Determined from DSC and Optical Textures^a

A. n (salen)VO						
←cooling (5 deg/min)						
n						
4		S _{C2}	81.8 (0.8)	S _{C1}	176.6 (3.6)	I
5		S _{C2}	77.9 (0.6)	S _{C1}	192.6 (3.8)	I
6				S _{C1} ^b	184.0 (3.3)	I
7		S _{C2}	50.2 (0.6)	S _{C1} ^c	188.4 (7.4) ^d	I
8	S _{C2}	62.4 (0.7)	S _{C1}	178.9 (2.9)	S _{C3}	198.2 (1.0) ^d I
10	S _{C2}	58.2 (0.2)	S _{C1}	165.3 (3.2)	S _A	209.3 (1.2) I
12	S _{C2}	71.3 (0.7)	S _{C1}	148.7 (2.4)	S _A	211.6 (1.2) I
B. n (salpn)VO						
heating (20 deg/min)→						
n						
6	K ₁	310.4 (8.1)	I _d			I _d
7	K ₁	160.1 (0.9)	K ₂	303.5 (10.9)		I _d
8	K ₁	168.6 (1.1)	K ₂	312.0 (11.4)		I _d
10	K ₁	166.2 (2.5)	K ₂	285.0 (15.7)		I _d
C. n (Me ₂ salpn)VO						
←cooling (5 deg/min)						
n						
5			S _{LC1} ^b	184.5 (5.3)		I
6	S _{LC2}	60.1 (2.1)	S _{LC1}	159.0–155.5 (12.6) ^{d,e}		I
7	S _{LC2}	40.7 (1.1)	S _{LC1}	150.5–149.4 (7.9) ^{d,e}		I
8	S _{LC2}	89.1 (5.3)	S _{LC1}	161.6–158.2 (6.6) ^{d,e}		I
10	S _{LC2}	100.2 (8.3)	S _{LC1}	149.1–146.6 (6.8) ^{d,e}		I
12	S _{LC2}	98.7 (17.0)	S _{LC1}	141.3–140.2 (7.4) ^{d,e}		I
14	S _{LC2}	96.8 (17.1)	S _{LC1}	139.8–137.8 (7.2) ^{d,e}		I

^aThe data for n (salen)VO and n (Me₂salpn)VO are obtained by cooling the isotropic phase, and for n (salpn)VO the data is obtained by heating crystals. Phase-transition temperatures (°C) are listed between the phases, and the transition enthalpies (kcal/mol) are in parentheses. S_{C1} and S_{C3} are fluid smectic C phases, S_{C2} is a nonfluid smectic C phase, K₁ and K₂ are crystal phases, I_d indicates that the compound melts to an isotropic phase with decomposition, S_{LC1} is a high-temperature fluid smectic phase with linear chain structure, and S_{LC2} is a lower temperature nonfluid smectic linear chain phase. ^bThis phase loses fluidity at lower temperatures. ^cThe S_{C1} and S_{C3} are observed to coexist around the phase-transition temperature, and the DSC thermogram shows two unresolved peaks which exhibit a pronounced scan-rate dependence. ^dMonotropic transition. ^eMultiple (3–5) smectic linear chain phases occur over this range which appear as unresolved DSC peaks at slow scan rates and as a single peak at scan rates of 10 deg/min or faster.

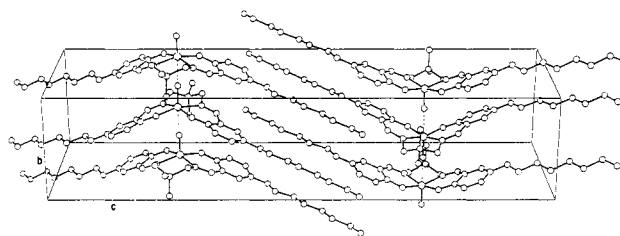


Figure 1. An ORTEP drawing of the unit cell of 7(Me₂salpn)VO viewed approximately down the a -axis. The linear chains (—V=O—·—V=O—)_n are oriented vertically and organize into highly interdigitated layers which are perpendicular to the plane of the paper. All of the linear chains in a given layer are pointing in the same direction to give ferroelectric organization within each layer. A bulk antiferroelectric structure results from the antiparallel organization of the linear chains in neighboring layers.

perature mesophase (S_{LC1}) causes the linear chain structure to reform with a V=O band at 875 cm⁻¹. Further cooling into the S_{LC2} phase at 36 °C produces an additional shift of 8 cm⁻¹ to lower energy, indicating that an even stronger linear chain structure is present in the low-temperature mesophase. Other members of the n (Me₂salpn)VO series were found to behave similarly.

X-ray powder diffraction and polarizing microscope analysis indicate that both of the main mesophases are smectics.⁸ The S_{LC1} phase is of low viscosity and exhibits a very smooth, well-defined focal conic texture. Cooling into the lower temperature S_{LC2} phase

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(13) For 7(Me₂salpn)VO, the V=O bond is 1.622 Å, whereas in the monomeric (salen)VO complexes, the V=O bond is 1.59 Å (ref 10).

(14) In CH₂Cl₂ solution n (Me₂salpn)VO species also exhibited a V=O of 987 cm⁻¹.

produces a pronounced graining and cracking, and the smooth texture is restored with reheating to S_{LC1} . The well-defined and smooth nature of the focal conic texture of the S_{LC1} phase is unusual for a polymeric material and necessitates facile splay deformations. These features and the high fluidity suggest that there is a low degree of position order between the linear chains and that the chains are quite flexible in this phase. However, X-ray studies on the S_{LC2} mesophase of $8(\text{Me}_2\text{salpn})\text{VO}$ indicate that positional order exists between the linear chains with major wide-angle diffraction peaks at 10.3, 9.1, 3.8, and 3.7 Å in addition to the lamellar peak at 20.2 Å.

In summary, we have developed a new type of unidirectional liquid crystalline polymer with a low-viscosity phase possessing supermolecular domains of polarization. These properties make these materials attractive candidates for poling into acentric states, and our initial experiments have indicated that the $n(\text{Me}_2\text{salpn})\text{VO}$ complexes are readily oriented to give a homogeneously ordered phase in fields of 10^3 V/cm.

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Registry No. 4(salen)VO, 138695-04-2; 5(salen)VO, 138695-05-3; 6(salen)VO, 138695-06-4; 7(salen)VO, 138695-07-5; 8(salen)VO, 138695-08-6; 10(salen)VO, 138695-09-7; 12(salen)VO, 138695-10-0; 5(Me_2salpn)VO, 138695-11-1; 6(Me_2salpn)VO, 138695-12-2; 7(Me_2salpn)VO, 138695-13-3; 8(Me_2salpn)VO, 138695-14-4; 10(Me_2salpn)VO, 138695-15-5; 12(Me_2salpn)VO, 138695-16-6; 14(Me_2salpn)VO, 138695-17-7; 6(salpn)VO, 138695-18-8; 7(salpn)VO, 138695-19-9; 8(salpn)VO, 138695-20-2; 10(salpn)VO, 138695-21-3.

Supplementary Material Available: Tables of crystal coordinates, thermal parameters, bond distances, and bond angles of 7(Me_2salpn)VO, graphs of phase transitions of all of the compounds reported, DSC data for 8(Me_2salpn)VO, VT-IR data, and X-ray powder diffraction data on the low-temperature phases of 8(salen)VO and 8(Me_2salpn)VO (15 pages). Ordering information is given on any current masthead page.

Deformation Density of a Diazirine Ring in the X-ray Structure of 3-[(*p*-Nitrophenoxy)methyl]-3-chlorodiazirine

T. Stanley Cameron,* Pradip K. Bakshi, and Bozena Borecka

Department of Chemistry
Dalhousie University
Halifax, Nova Scotia, Canada B3H 4J3

Michael T. H. Liu*

Department of Chemistry
University of Prince Edward Island, Charlottetown
Prince Edward Island, Canada C1A 4P3

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The chemistry of the diazirines has a relatively short history, dating from the discovery of these compounds in 1960. The past 30 years have seen a high level of activity in the study of their chemistry, with advances in the field being regularly reviewed.¹⁻⁵

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Table I. Comparison of Bond Lengths and Angles in Diazirines⁷

compound	bond lengths (Å)		bond angle (deg) N—C—N
	N=N	C—N	
(C ₁₀ H ₇ CH ₂)ClCN ₂	1.244 (10)	1.465 (10)	50.3 (5) ^a
MeClCN ₂	1.241 (5)	1.462	50.2 (5)
MeBrCN ₂	1.240 (5)	1.462	50.2
(Me) ₂ CN ₂	1.235 (5)	1.490 (10)	48.9
MeHCN ₂	1.235 (5)	1.481 (10)	49.3 (3)
F ₂ CN ₂	1.293 (9)	1.426 (4)	53.9 (4)
H ₂ CN ₂	1.228 (3)	1.482 (3)	48.9
this work	1.229 (3)	1.460 (1)	49.8 (1) ^a

^aDimensions derived from single-crystal X-ray diffraction. Other dimensions derived from rotational spectra.

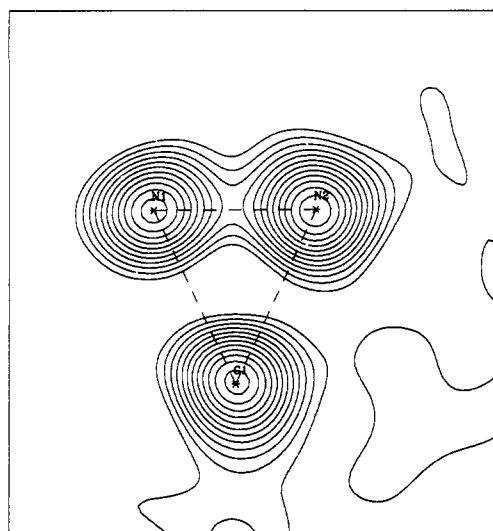
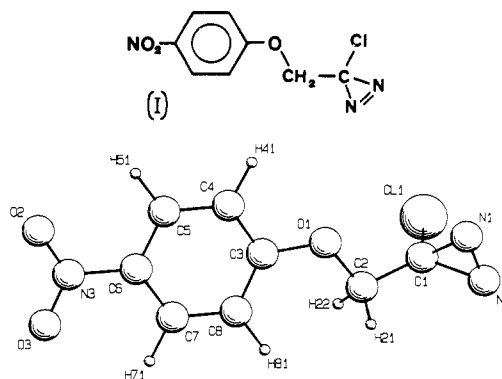


Figure 1. F_0 map through the plane of the diazirine ring. Contours are at $0.5 e/\text{Å}^3$.

Curiously, apart from the structure of a hetero dimetal complex,⁶ only one X-ray structure of a free diazirine ring has been reported,⁷ and this compound decomposed in the X-ray beam, even at low temperatures. We report here the structure of 3-[(*p*-nitrophenoxy)methyl]-3-chlorodiazirine (I), a remarkably stable compound with such a good crystalline form that it has been possible to collect low-temperature X-ray data of a quality suitable for deformation electron density studies.



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