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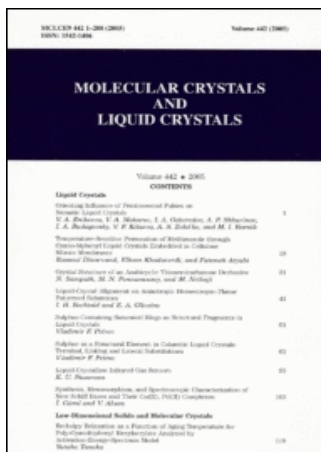
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MOLECULAR CRYSTALS AND LIQUID CRYSTALS

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Molecular Crystals and Liquid Crystals

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Design of New Stable Radicals for Molecular Magnetic Materials

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DESIGN OF NEW STABLE RADICALS FOR MOLECULAR MAGNETIC MATERIALS

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Abstract A series of new heterocyclic stable free radicals based on the thioaminyl fragment **1** was designed in order to introduce a π -delocalized spin to the rigid cores of mesogenic molecules. The design allows for preparation of calamitic and discotic liquid crystals. Computational analysis and first experimental results of the radicals (ESR) are presented.

INTRODUCTION

The thioaminyl group¹ (**1**) has been featured as a structural element of chemically and thermally stable organic free radicals (Figure 1). Almost all species derived from **1** are π -delocalized radicals with the odd electron in the anti-bonding orbital, and they form acyclic compounds²⁻⁵ such as **2-5**, and also cyclic derivatives⁶⁻¹⁰ such as **6-10** and **11-14**. Some of these radicals melt above 150 °C without decomposition,² some exist as liquids⁹ and some have been explored as possible unidimensional conductors,¹¹⁻¹⁴ and molecular magnetic materials.¹² For instance, radical **3** and its *meta* isomer show weak antiferromagnetic interactions¹⁵ but in a similar compound with chlorine atoms as substituents weak ferromagnetic interactions have been observed.¹⁶ Another study involving derivatives of **10** revealed^{12,13} that they behave as diamagnetic substances in the solid phase with some paramagnetic impurities (<1%). In the liquid phase, however, the magnetic moment ($\chi_g=4.8 \times 10^{-6}$ cgs) of radical **9** is essentially temperature independent. The antiferromagnetic spin-spin exchange in the solid phase has been attributed to the dimerization at the sulfur center and formation of a weak S-S bond (e.g., $\Delta H_{\text{dimer}}=-37 \pm 3$ kJ/mol for **7**⁹).

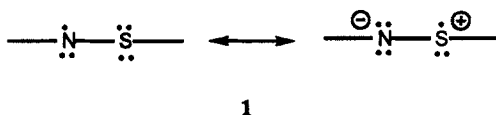
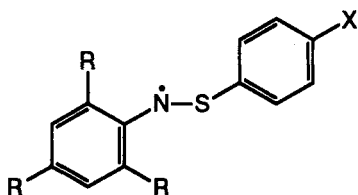
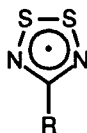


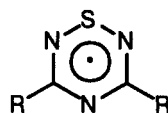
FIGURE 1 Resonance structure of thioaminyl radical fragment (**1**).



- 2 R=Ph; X = Halogen
 3 R=Ph; X = NO₂
 4 R=Ph; X = CH₃
 5 R=*t*-Bu; X = NO₂



- 6 R=Halogen
 7 R=CF₃
 8 R=CH₃
 9 R=*t*-Bu
 10 R=Ph



- 11 R=Cl
 12 R=CF₃
 13 R=Ph
 14 R=C₆H₄-4-NO₂

The unparalleled structural versatility of the thioaminy fragment and the possibility of introducing it into a variety of aromatic ring systems make it a logical centerpiece in the design of new cyclic radicals in which the electronic effects can be engineered. This, in turn, opens possibilities for the design and synthesis of an unprecedented class of liquid crystals (LC) with a delocalized neutral π -radical in the rigid core, if some additional geometrical requirements¹⁷ are met. For instance, a typical calamitic liquid crystal molecule has an elongated shape and consists of a rigid core and a flexible tail; a discotic liquid crystal molecule consists of a disc-like rigid core with radially distributed flexible tails¹⁸ (Figure 2). These materials, while being liquid-like, exhibit some characteristics of ordered crystalline solids, e.g., optical and magnetic anisotropy.^{17,19} The degree of crystallinity varies in different structures: nematics are more liquid-like (least oriented), while smectics and discotics are highly oriented or more crystalline (Figure 2). The relative orientation of molecules and resulting interactions vary in different mesophases (e.g., in going from a smectic to a nematic phase) and even within a given mesophase (e.g., smectic C phase in which the tilt angle is a function of temperature). These seemingly minute differences in laminar structure are crucial for the overall bulk properties of the material.

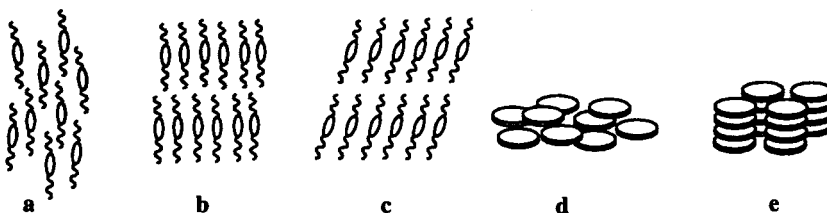
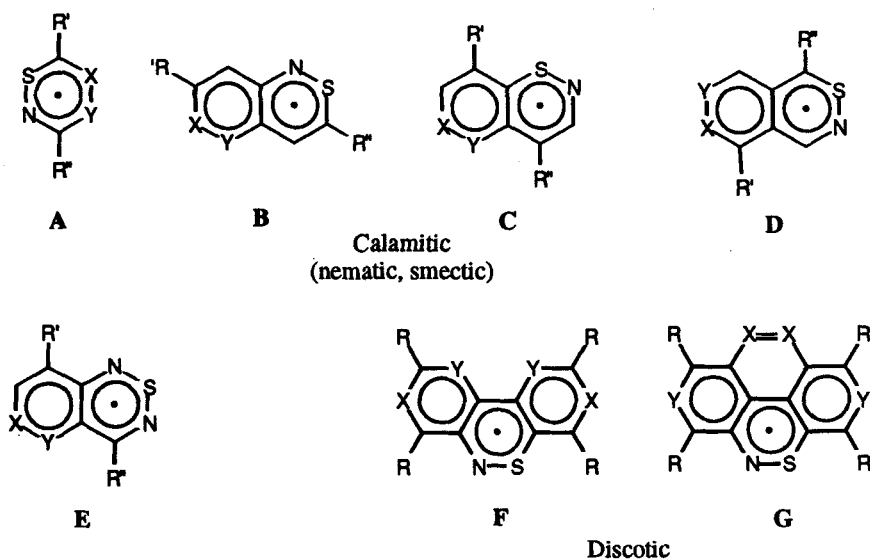


FIGURE 2 Molecular arrangements in different liquid crystals: a) nematic b) smectic A, c) smectic C, d) nematic discotic, e) columnar discotic. The ovals represent the rigid cores of the molecules and the lines are the flexible tails.

Since magnetic behavior of the molecular material and its physical properties strongly depend on contact between molecules and orbital-orbital interactions, it is expected that the long range molecular order characteristic for LC will play an important role.^{20,21} In multiphase LC incorporating such a π -radical system, the anticipated extended lateral spin-spin interactions should result in significant changes in magnetic behavior associated with different molecular arrangements (Figure 2).

The majority of LC with permanent spins studied thus far include metallomesogens in which the spin originates from transition metal centers.²²⁻²⁴ Most of the spin density resides on the metal center, some is distributed into the ligand *via* a polarization mechanism, but almost none is transferred to the π -system. This limits the intermolecular interaction and spin-spin magnetic exchange. There are very few LC containing an organic spin in the structure, and the only π -radical compounds are derivatives of bipyran-4,4'-ylidene, which form charge transfer discotic LC upon treatment with TCNQ.^{25,26} Other sources of organic radicals are not suitable for the synthesis of LC primarily due to inappropriate geometry and bulkiness (e.g., nitroxyl radicals^{21,27,28}) or substitution patterns (e.g., 10 and 13).



X, Y = N, CH; R = 4-alkylphenyl, alkoxyphenyl; R', R'' = alkyl, cycloalkyl, aryl

FIGURE 3 Schematic representation of several possible radical structures suitable for the preparation of liquid crystals.

In this paper we present a general design for a new class of liquid crystals, both calamitic (A-E) and discotic (F,G), incorporating new cyclic π -radicals in the rigid cores (Figure 3).

RESULTS AND DISCUSSION

The Design

The general prescription for magnetic LC is based on two principles:

- linear or disc-like molecular shape with a rigid core (geometrical anisotropy)
- incorporation of the two-atom fragment **1** into the rigid core.

The remaining unsubstituted atoms in the cyclic core can be either CH fragments or nitrogen atoms. It is expected that the N derivatives will further stabilize the unpaired spin. The introduction of nitrogen atoms opens possibilities for formation of metal complexes of, e.g., F (Y=N), which may or may not be LC. Unlike that in other structures, the substitution pattern in E allows for two nitrogen atoms next to the sulfur center and the formation of the N-S-N link characteristic for stable radicals **11-14** and several others.²⁹

TABLE I. Experimental and calculated data for **7** and **12**.

	Experimental		Calculated (UHF)		
			MNDO	AM1	PM3
Compound 7					
IP [eV]	8.25 ^a		10.24	9.86	10.31
<i>molecular structure</i>					
	<u>Gas Phase^b</u>		<u>X-ray Diffr.^b</u>		
S-S [Å]	2.113	2.082	1.992	1.981	1.896
S-N ave [Å]	1.623	1.630	1.604	1.596	1.717
N-C ave [Å]	1.318	1.316	1.357	1.358	1.355
Compound 12					
IP [eV]	9.1 ^a		10.91	9.99	10.49
<i>molecular structure</i>					
Compound 13					
	<u>X-ray Diffr.^c</u>				
S-N ave [Å]			1.617	1.606	1.703
C-NS ave [Å]			1.324	1.346	1.350
C-NC ave [Å]			1.335	1.383	1.379

^aBoere, R. T.; Oakley, R. T.; Reed, R. W.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1989**, *111*, 1180. ^bHöfs, H.-U.; Bats, J. W.; Gleitern, R.; Hartmann, G.; Mews, R.; Eckert-Maksic, M.; Oberhammer, H.; Sheldrick, G. M. *Chem. Ber.* **1985**, *118*, 3781. ^cHays, P. J.; Oakley, R. T.; Gordes, A. W.; Pennington, W. T. *J. Am. Chem. Soc.* **1985**, *107*, 1346.

The choice of substituents is rather typical for a mesogenic material, and it depends on spin distribution within the heterocyclic ring (control of spin delocalization and spin reactivity). However, there is a juxtaposition of two opposing factors:

- maximum intermolecular orbital overlap (minimum steric hindrance)
- stabilization of radicals and prevention of dimerization (steric hindrance).

This leads to a delicate balance between magnetic interactions, stability of the radicals, and mesogeneity of the compounds.

Computational Analysis

The choice of calculation method was determined by closest agreement between experimental (PES and molecular structure) and calculated results (MNDO, AM1 and PM3)³⁰ for the model systems 4-trifluoromethyl-1,2,3,5-dithiadiazolyl⁶ (**7**) and 3,5-bis(trifluoromethyl)-1,2,4,6-thiatriazinyl⁷ (**12**) radicals. Good agreement between calculated (MNDO/RHF) and experimental (PES) ionization potential and hyperfine coupling constant has been shown for both radical systems.⁷ The more reliable *ab initio* methods are less applicable because of the large size of molecules. Computational results for **7** and **12** are summarized in Table I.

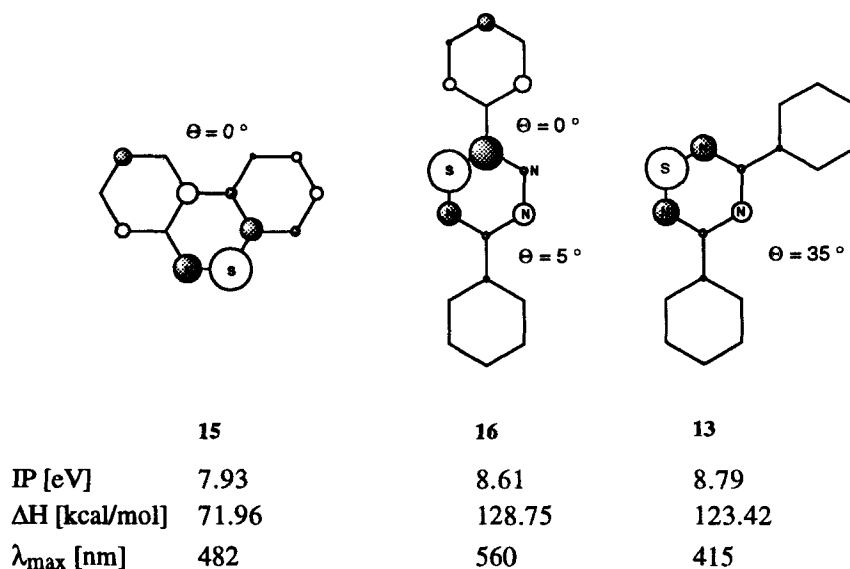


FIGURE 4 AM1/UHF calculated SOMO coefficients, ionization potential (IP), enthalpy of formation (ΔH), maximum of long wavelength absorption (λ_{\max}), and dihedral angle (Θ) of the two aromatic rings.

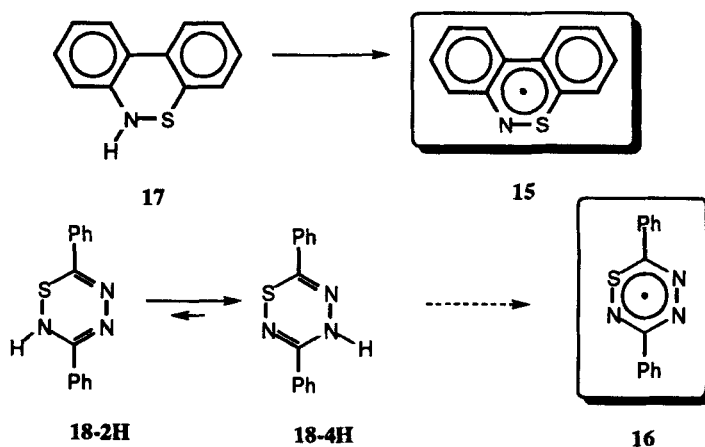
Although AM1 and MNDO results compare favorably with experiment, the more advanced AM1/UHF method has been selected for calculation of over a dozen new heterocyclic radical systems derived from structures A-G.³¹ Compounds **15** and **16** (derivatives of **F** and **A**, respectively) were chosen as the first synthetic targets mostly because of their similarity to known compounds, predicted stability, and synthetic feasibility. Incorporation of nitrogen atoms in positions 4 and 5 of **16** should chemically stabilize the radical. The calculated SOMO and enthalpy of formation of these two radicals are shown in Figure 4. The corresponding properties of known¹⁰ radical **13** are also shown here for comparison.

The antibonding SOMO orbital is localized mostly on the thioaminy fragment (Figure 4), thus, dimerization of the radical in these systems *via* a sulfur-sulfur bond formation, as observed¹⁰ in **13** and others, can be anticipated. A large SOMO coefficient on the carbon adjacent to sulfur in **16** permits further delocalization into the phenyl substituent, which is not the case in its formal "meta" analog, radical **13**. The "para" radical **16** has predicted lower thermodynamic stability than **13** by over 5 kcal/mol.

Calculated λ_{\max} of long wavelength absorption for radical **13** agrees with its observed yellow color.¹⁰ The predicted values of excitation energies for radicals **15** and **16** suggest orange and violet colors, respectively (Figure 4).

Synthesis

Sulfenamide **17** was obtained according to a modified literature procedure.³² The synthesis of compound **17** and compound **18**, a derivative of the experimentally unknown³³ 1-thia-2,4,5-triazacyclohexane ring system, will be described elsewhere (Scheme 1).³⁴



Scheme 1

Conversion of the sulfenamides to radicals can be achieved either by one-electron oxidation and deprotonation, or by two-electron oxidation to iminosulfinyl chloride followed by one-electron reduction with Ph_3Sb (Figure 5).

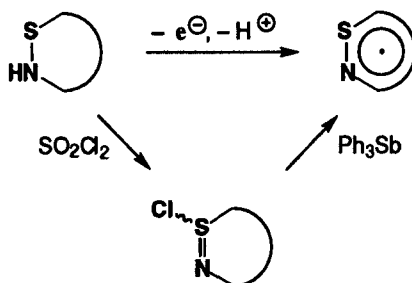


FIGURE 5 General methods for generation of thioaminy radicals.

Structural Evidence

X-ray analysis³⁵ of precursor **18** shows that its preferred form in the solid state is the 4H rather than the 2H form (Figure 6). The AM1 calculations predict the 4H tautomer to be more stable than 2H by 1.35 kcal/mol. The heterocyclic ring in **18-4H** is highly distorted from planarity because of the anti-aromaticity associated with eight π -electrons.

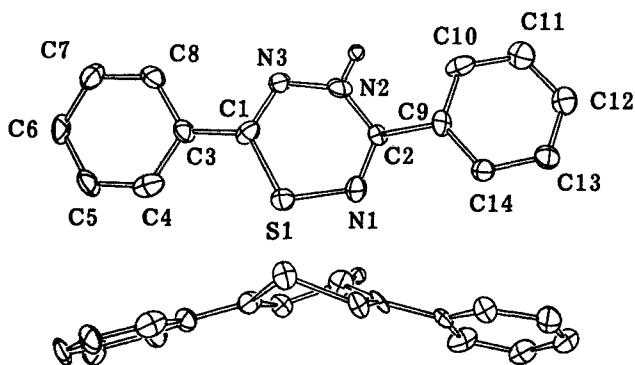
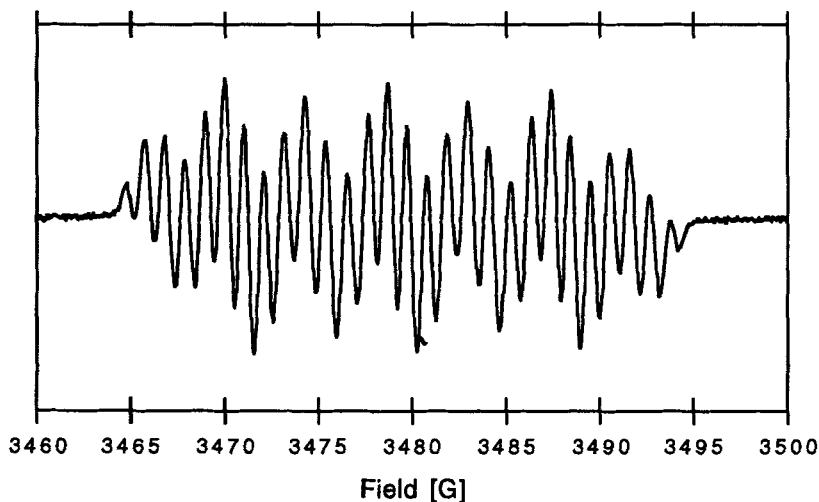


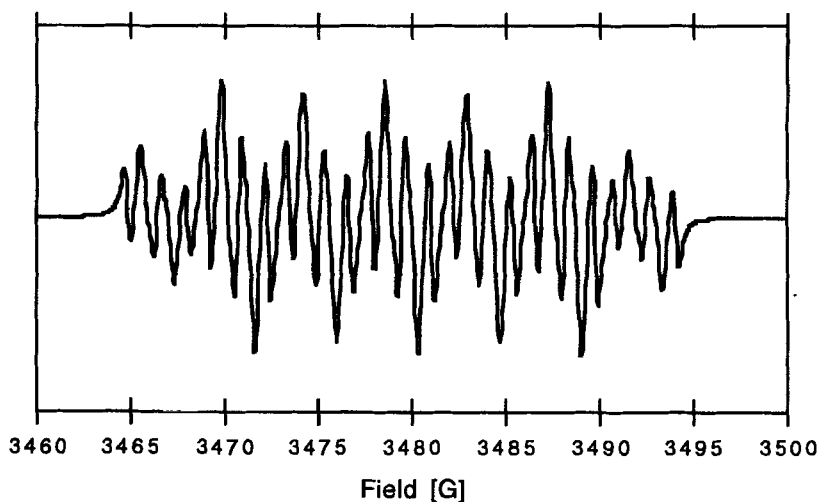
FIGURE 6 ORTEP perspective drawings of **18-4H** showing 50% thermal ellipsoids and the atomic-labeling scheme. Pertinent experimental and calculated (in brackets) distances (\AA) are as follows: S(1)–N(1), 1.73 (1) [1.64]; N(1)–C(2), 1.28 (1) [1.30]; C(2)–N(2), 1.37 (1) [1.46]; N(2)–N(3), 1.40 (1) [1.35]; N(3)–C(1), 1.30 (1) [1.32]; C(1)–S(1), 1.76 (1) [1.75].

Electrochemical Analysis

Cyclic voltametry of precursors **17** and **18** has shown oxidation peaks at 0.50 V and 1.05 V, respectively, vs SCE electrode in CH_2Cl_2 solution containing one equivalent of pyridine. This relative order of the redox potentials corresponds to the order of calculated (AM1) ionization potentials for **17** and **18**, which are 7.97 eV and 8.16 eV, respectively.



a



b

$a(\text{N})=8.70$, $a(\text{H})=4.30$, $a(\text{H})=4.25$, $a(\text{H})=1.32$, $a(\text{H})=1.05$, $a(\text{H})=0.82$

FIGURE 7 ESR spectrum of 10-aza-9-thiaphenanthryl radical (**15**) recorded in CH_2Cl_2 (a) and simulated (b) using the listed above hyperfine coupling constants [G].

Generation of Radicals and ESR Spectroscopy

Precursors **17** and **18** were treated with thianthrene radical cation perchlorate salt ($E_{1/2}=1.30$ V)³⁶ in dry CH_2Cl_2 containing 1 equivalent of pyridine. In both cases, immediate disappearance of the purple color of the oxidant was observed, but only **17** formed a persisting radical whose ESR spectrum is shown in Figure 7a. The intensity of the signal remained unchanged for 1 hr at 25° C under inert atmosphere, but it disappeared completely after one week, and a purple solution was formed. Based on observations of the chemical reactivity of **17**, it appears that the radical undergoes an acid catalyzed decomposition and formation of an unidentified purple product. Oxidation of the precursors with PbO_2 in benzene was not successful and no ESR signal was observed.

The experimental spectrum was simulated using hyperfine coupling constants shown in Figure 7 which qualitatively agree with the calculated hydrogen spin densities in **15** (Figure 8). It is noteworthy that AM1/CI calculations performed very poorly on π -spin distribution in **15**.

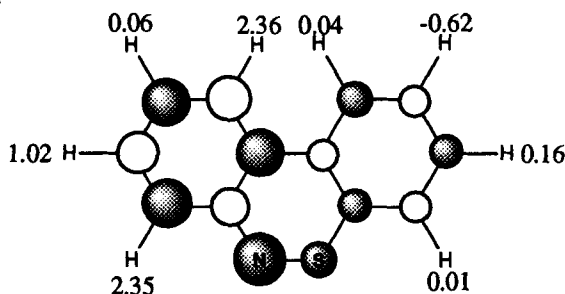


FIGURE 8 Calculated (AM1/UHF) distribution of π spin density in **15** (p_z orbital) represented by circles, and (AM1/CI) spin densities on hydrogen atoms ($\times 10^4$).

CONCLUSIONS

A new class of heterocyclic radicals presented here promises for the first time a general access to magnetic LC with π -delocalized spin. Persisting radical **15** constitutes the first experimental result and we are now pursuing a family of discotic LC based on it. We are also actively investigating stability of radical **16** and the possibility of synthesis of calamitic LC based on it.

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