Cyclopenta-1,2-dithioles, Cyclopenta-1,2-thiazines, and Methylenoindenes from New Molecular Rearrangements

Oleg A. Rakitin

N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences, Leninsky Prospect, 47, Moscow B-334, Russia

Charles W. Rees* and David J. Williams

Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, U.K.

Tomás Torroba

Departamento de Química Orgánica, Facultad de Veterinaria, Universidad de Extremadura, 10071 Cáceres, Spain

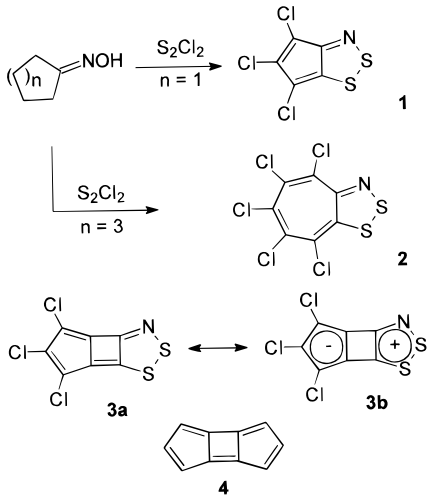
Received June 28, 1996[⊗]

The cyclobutanone oxime **6** reacts with disulfur dichloride, *N*-chlorosuccinimide, and Hünig's base to give three unexpected 10 π pseudoazulenes in low yield: the dark blue cyclopenta-1,2-dithiole **7**, its red isomer **10**, and the orange cyclopenta-1,2-thiazine **8**. The benzo derivative **14** of oxime **6** gives an analogous benzo product **15** together with the methylenoindene **16** in high yield. The formation of all of these products can be explained by a unified mechanism based on initial abnormal Beckmann rearrangement of the oximes to cyanides followed by cyclization and/or exhaustive chlorination and dehydrochlorination. The 1,2-dithiole **7** is synthesized independently from 1-(cyanomethyl)cyclopentene **11** and the above reagents, and 1-cyanomethylindene **17** is similarly converted into methylenoindenes **18** and **19**, which are isomers of product **16**. Structures **7** and **15** are confirmed by X-ray crystallography, and compounds **7**, **8**, **15**, **16**, **18**, and **19** show birefringence on heating in a hot stage polarizing microscope indicating, most unexpectedly, liquid crystalline behavior.

Introduction

Much of the search for new materials has focused on sulfur heterocycles since the discovery of superconducting tetrathiafulvalene charge-transfer complexes[1] and molecular switches,[2] thiazole and thiadiazole liquid crystals,[3] and thiophene nonlinear optical materials.[4] A good source of new sulfur-bearing structures with potentially attractive characteristics yet to be exploited are pseudoazulenes.[5] Many of these are still unknown or poorly studied, and new methods for their synthesis are required. We have previously described a remarkably extensive transformation of simple saturated oximes with disulfur dichloride, S_2Cl_2, into fully unsaturated and chlorinated heteroaromatic systems.[6] Thus, cyclopentanone oxime gave the deep violet 4,5,6-trichlorocyclopenta-1,2,3-dithiazole **1** with S_2Cl_2 and Hünig's base in tetrahydrofuran (THF) at 4 °C; the addition of *N*-chlorosuccinimide (NCS) supplemented the spontaneous ring chlorination and improved the yield of **1**. Similarly, cycloheptanone oxime gave the red pentachlorocycloheptadithiazole **2**. These two reactions involve the formation of seven and 10 new bonds, respectively, and a detailed mechanism was proposed for them based upon the activation to chlorodeprotonation of all the carbocyclic ring positions by the two sulfur atoms. Evidence was presented for the 10π and 12π delocalized electronic structures of **1** and **2**, respectively.[6]

In connection with our studies on pseudoazulene cyclopentadithiazoles, we hoped to extend this reaction to the synthesis of the novel tricyclic species **3**, a heterocyclic derivative of the unknown hydrocarbon **4**[7] and isoelectronic with the dianion of **4**. Compound **3** can also be considered as an analogue of biphenylene with two 6π aromatic rings fused to a four-membered ring, **3b**.



When we applied the same reaction conditions to bicyclic cyclobutanone oximes, by analogy with the formation of compounds **1** and **2** above, we discovered a

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1996.

(1) Williams, J. C.; Schultz, A. J.; Geiser, U.; Carlson, K. D.; Kini, A. M.; Wang, H. H.; Kwok, W. K.; Whangbo, M. H.; Schirber, J. E. *Science* **1991**, *252*, 1501. (b) Bryce, M. R. *Chem. Soc. Rev.* **1991**, *20*, 355. (c) Garín, J. *Adv. Heterocycl. Chem.* **1995**, *62*, 249.

(2) Jørgensen, T.; Hansen, T. K.; Becher, J. *Chem. Soc. Rev.* **1994**, *23*, 41.

(3) Day, P.; Bradley, D. C.; Bloor, D. *Molecular Chemistry for Electronics*; The Royal Society: London, 1990; p 1. (b) Gray, G. W. *Phil. Trans. R. Soc. London* **1990**, *A 330*, 73.

(4) Jen, A. K. Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 90.

(5) For a review on pseudoazulenes, see: Timpe, H-J.; El'tsov, A. V. *Adv. Heterocycl. Chem.* **1983**, *33*, 185.

(6) Plater, M. J.; Rees, C. W.; Roe, D. G.; Torroba, T. *J. Chem. Soc., Chem. Commun.* **1993**, 293; *J. Chem. Soc., Perkin Trans. 1* **1993**, 769.

(7) Bister, H. J.; Butenschön, H. *Synlett.* **1992**, 22.

S0022-3263(96)01223-6 CCC: $12.00

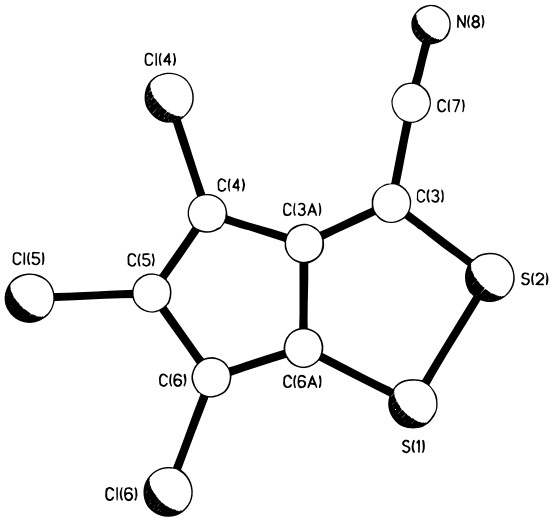
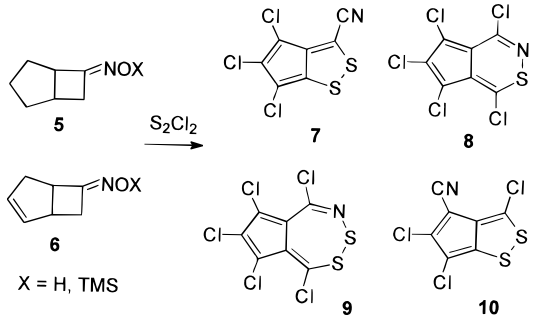


Figure 1. Molecular structure of 4,5,6-trichlorocyclopenta-1,2-dithiole-3-carbonitrile (**7**).

completely new set of molecular rearrangements giving rise to new heterocyclic systems.[8] In this paper, we give a detailed description of the conditions for control of the nature and yield of the products that are obtainable from the reactions of bicyclic cyclobutanone oximes and their benzo derivatives with disulfur dichloride.

Results and Discussion

When *cis*-bicyclo[3.2.0]heptan-6-one oxime (**5**)[9] or its *O*-trimethylsilyl derivative was treated with S_2Cl_2, Hünig's base, and NCS in THF a dark blue crystalline compound **7** was obtained in low yield. With the analogous unsaturated oxime **6**,[9] or its *O*-trimethylsilyl derivative, compound **7** was again formed in similar yield, together with a less polar orange crystalline compound **8**.



NMR spectroscopy and mass spectrometry showed **7** to be $C_7Cl_3NS_2$ with seven different carbon atoms, and the infrared spectrum showed a cyano group at 2218 cm^{-1}. The dark blue compound was established as 4,5,6-trichlorocyclopenta-1,2-dithiole-3-carbonitrile (**7**) by X-ray structure determination (Figure 1). Thus, the 10π pseudoazulene system **7** was formed, by an extensive rearrangement, rather than the expected 12π system **3**. The only other example of this ring system, 4,6-di-*tert*-butylcyclopenta-1,2-dithiole, is air sensitive,[10] while compound **7**, even without the *tert*-butyl groups, is perfectly stable.

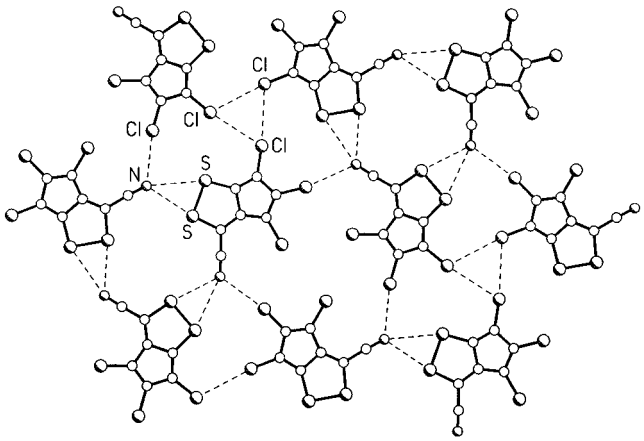


Figure 2. Molecular packing of 4,5,6-trichlorocyclopenta-1,2-dithiole-3-carbonitrile (**7**).

Despite its dark color, compound **7** showed strong birefringence upon melting in a hot stage polarizing microscope; heating its crystals placed between crossed polarizers showed a transition to a mesophase of mosaic texture before melting. Although compound **7** was not expected to have this characteristic, its X-ray diffraction analysis showed that the molecules of **7** are packed in layers with virtually no interaction between the layers. The molecules inside the layer showed strong intermolecular attractions, as evidenced by the short distances between selected atoms of molecules belonging to the same layer (Cl−Cl, 3.38 Å, N−Cl, 3.03 Å, N−S, 3.03 and 3.24 Å). The packing of **7** is shown in Figure 2. It is therefore assumed that heating crystals of **7** first relaxes the packing between the layers, giving rise to a mesophase that keeps the order within the layers until thermal disorder at a higher temperature relaxes the internal structure of the layers upon melting. This would explain the thermotropic liquid crystal behavior of compound **7**.

Compound **8** was shown to be C_7Cl_5NS by NMR spectroscopy and mass spectrometry. It did not have a cyano group in the infrared spectrum, suggesting that the nitrogen was part of a heterocyclic ring; on mechanistic grounds and by analogy with compound **15** (see below), it was assigned the 10π aromatic pentachlorocyclopenta[*d*]-1,2-thiazine structure **8**, a new pseudoazulene system. This compound also showed birefringence in a hot stage polarizing microscope at temperatures under that required for transition to an isotropic liquid. The causes of liquid crystalline behavior are probably similar to those for **7**. Monitoring these reactions by TLC showed that compound **8** appeared in the reaction mixture when it was kept for at least 3 days at 4 °C, but product **7** appeared in the final stage of the reaction when it was refluxed in THF for 4 h. If the reaction mixture was refluxed at the beginning, or if the NCS was omitted, no pure products could be isolated.

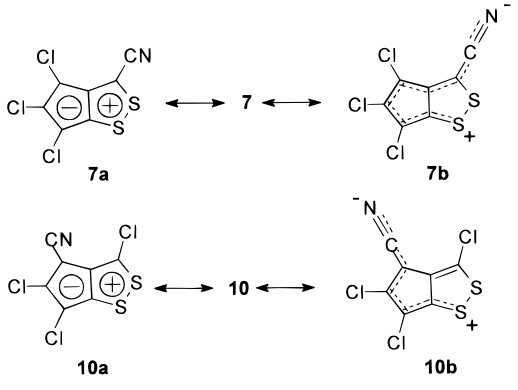
In some runs, by methods A or F (see Experimental Section), a turquoise-blue compound, very close to compound **8** on TLC, could be isolated in minute amounts. This new compound **9** showed exactly the same mass spectrum as compound **8**, and its ^{13}C NMR spectrum was also very similar to that of **8**. Although the molecular mass peak of compound **9** could not be seen in the MS spectrum under electron impact, the chemical ionization MS using ammonia afforded cluster ion peaks at 373, 375, 377, 379, whose isotopic abundances corresponded

(8) Rakitin, O. A.; Rees, C. W.; Torroba, T. *J. Chem. Soc., Chem. Commun.* **1996**, 427.
(9) Ghosez, L.; Montaigne, R.; Roussel, A.; Vanlierde, H.; Mollet, P. *Tetrahedron* **1971**, *27*, 615.
(10) Hafner, K.; Stowasser, B.; Sturm, V. *Tetrahedron Lett.* **1985**, *26*, 189.

to five chlorine atoms in the structure. The ion $C_7Cl_5NS_2NH_3NH_4^+$ expected for **9** should give peaks at 372, 374, 376, and 378, which are closely related to those observed, except for the difference of one unit of mass. These facts, and the close similarity between the IR and NMR spectra of **8** and **9**, suggested structure **9**. This unstable compound should readily extrude sulfur[11] to afford **8**.

Furthermore, the oxime−S_2Cl_2 reaction was very sensitive to the quality of the sulfur reagent. Thus, addition of impure S_2Cl_2 or of SCl_2 to the reaction mixture slightly increased the yield of **8** but dramatically decreased the yield of **7** and gave instead a new amorphous red product **10**. Despite the differences in color and polarity, compound **10** was shown by IR and NMR spectroscopy and mass spectrometry to be an isomer of **7**. Linked scan mass spectrometry of **10** showed a strong tendency to lose a C=S group from the fragment [M^+ − Cl], confirmed by HRMS, and a weak tendency to lose a Cl−C=S fragment from the molecular peak. This strongly suggested the isomeric structure **10** for this product. Compound **10** did not show birefringence upon melting between crossed polarizers. It is a stable solid in the absence of moisture, but it is rather unstable in solution in common solvents.

Although the differences in color and polarity between the structurally very similar isomers **7** and **10** are, at first sight, surprising, they can be rationalized when the delocalized nature of the ring system is considered. We believe that there is a 10π aromatic (pseudoazulene) contribution (e.g., **7a**) in which each ring can attain 6π aromatic character, leading to the overall polarity shown. It is then reasonable that the powerfully electron-withdrawing cyano group will have a substantially different influence from the 3-position (in the less polar compound **7**) where it is opposing and from the 4-position (in the more polar isomer **10**) where it is reinforcing the polarity of the ring system (e.g., **10a**).[12] The UV/vis spectra of **7** and **10** in dichloromethane are very similar, except that the spectrum of **7** is shifted to longer wavelength, with respect to the spectrum of **10**, thus explaining the different color of each isomer (Figure 3). The more extended delocalization of **7**, responsible for the bathochromic shift, is probably due to the extended conjugation form **7b**, for which there is no counterpart in compound **10** (e.g., **10b**).



Despite considerable variation in the oxime−S_2Cl_2 reaction conditions (methods A−F in the Experimental Section), the yields of **7**, **8**, and **10** were always low, and none of the expected product **3** was obtained (see Table 1).

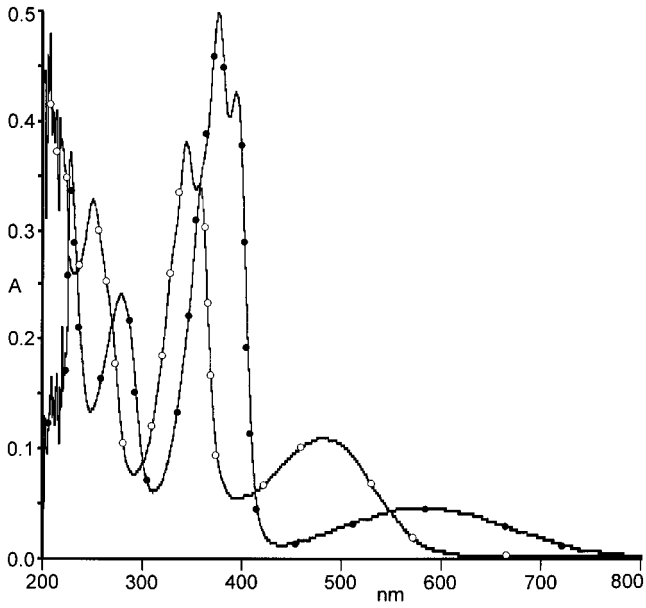
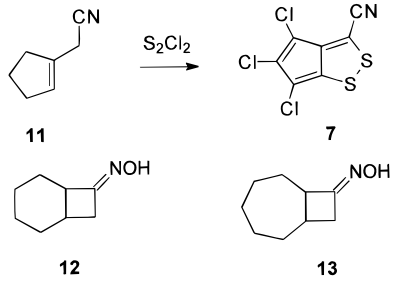


Figure 3. Electronic spectra (absorbance vs wavelength (nm)) of **7** (●) and **10** (○) in dichloromethane at 3.7×10^{-5} mol L^{-1}.

Table 1. Yields of Compounds 7, 8, and 10 Obtained from Reaction of 5 or 6 and S_2Cl_2 in Different Conditions

compd	X	method	reflux time (h)	**7** (%)	**8** (%)	**10** (%)
6	H	A	4	10	5	
6	TMS	C*	3.5	4	4	
6	TMS	C	4	13		
6	H	F	4	6	5	13
6	H	F*	4		10	10
5	TMS	C	4	9		
5	H	F	4		5	15

Given the cyclopentadithiole structure for product **7**, a more rational synthesis would start from 1-(cyanomethyl)cyclopentene (**11**).[13] Treatment of this with S_2Cl_2, Hünig's base, and NCS in THF afforded compound **7** in better yield (20%).



Two related bicyclic cyclobutanone oximes did not give clear results. Thus, the reaction of *cis*-bicyclo[4.2.0]octan-7-one oxime (**12**)[9] and disulfur dichloride afforded neither isolable products nor detectable intermediates as judged from TLC. It is worth noting that this oxime cannot give delocalized 10π pseudoazulene products analogous to **7**, **8**, and **10**. When *cis*-bicyclo[5.2.0]nonan-8-one oxime **13**[14] was treated with disulfur dichloride, a purple amorphous solid, unstable in solution in common solvents, was

(11) For a recent review on sulfur extrusion, see: Bohle, M.; Liebscher, J. *Adv. Heterocycl. Chem.* **1996**, *65*, 39.

(12) R_f's for **7** and **10** were measured on Merck 60 F_{254} silica TLC precoated plates with petroleum ether−dichloromethane (1:1 v/v) as eluent. R_f for **7** = 0.60; R_f for **10** = 0.29.

(13) Masamune, T.; Sato, S.; Abiko, A.; Ono, M.; Murai, A. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2895.

(14) Wiberg, K. B.; Nakahira, T. *J. Am. Chem. Soc.* **1971**, *93*, 5193.

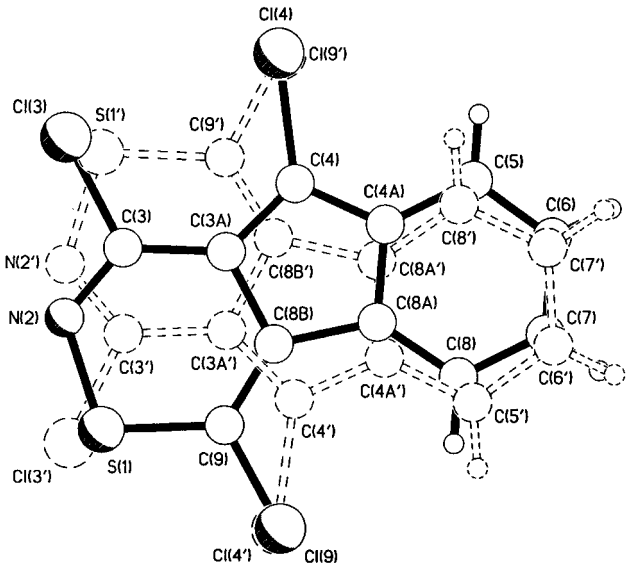
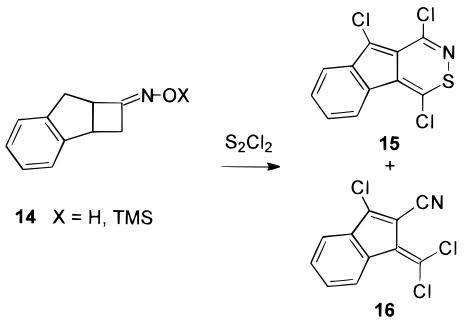


Figure 4. Molecular structure of 3,4,9-trichloroindeno[2,1-*d*]-1,2-thiazine (**15**) showing the C_2 disorder present in the crystals.

obtained. Although the HRMS showed a molecular mass peak that corresponded to one of the expected products, $C_9HCl_4NS_2$, the instability of the compound rendered IR and NMR spectroscopy and microanalysis impossible. It is also notable that the analogous products from this oxime, vinylogs of **7**, **8**, and **10**, would be 12π antiaromatic systems and possibly too unstable to survive.

We next investigated the reaction of the benzo analogue **14** of oximes **5** and **6** with S_2Cl_2, seeking the benzo derivatives of the two products **7** and **8**. Two stable yellow crystalline compounds **15** and **16** were formed from the oxime and its *O*-trimethylsilyl derivative.



The orange compound **15**, $C_{11}H_4Cl_3NS$, was the benzo analogue of **8**. The structure of this compound was confirmed by X-ray crystallography as the 1,4,9-trichloroindeno[2,1-*d*]-1,2-thiazine (**15**), although molecular disorder in the crystal prevented the accurate resolution of the structure. The molecular structure of compound **15** is shown in Figure 4. As in previous examples, compound **15** showed birefringence in a hot stage polarizing microscope when heated below its melting point.

The second product, $C_{11}H_4Cl_3N$, did not contain sulfur but had a nitrile absorption at 2226 cm^{-1} and was assigned the structure 1-(dichloromethylene)-3-chloroindene-2-carbonitrile (**16**) on spectroscopic grounds. This compound showed birefringence below its melting point when it was heated between cross polarizers, having more than one transition between phases. The second mesophase, showing a broken fan-shaped texture,[15] was reached by heating the solid as well as by cooling the isotropic liquid. This unexpected fact is not explicable on the basis of similarity to the previous examples, and further evidence is being sought for the characterization of the mesophase of this and the isomeric compounds (see below).

Table 2. Yields of Compounds 15 and 16 Obtained from Reaction of 14 and S_2Cl_2 in Different Conditions

X(**14**)	method	reflux time (h)	**15** (%)	**16** (%)
H	A	4.5	15	32
H	B	3.5	45	25
H	A	2.5	9	48
CONHPh	E	3.5	5	7
TMS	C	3.5	10	78
TMS	D	3	33	62
TMS	D*	2.5	3	3
TMS	D	2.5	28	30
TMS	D	1.5	12	18

The reaction of **14** with S_2Cl_2 was very sensitive to the conditions employed, and the nature of the *O*-substitution in the oxime group was especially important, permitting the selective preparation of either compound as the main product of the reaction (see Table 2). A stable protecting group on the oxime (**14**, X = CONHPh) resulted in very low yields of **15** and **16**. The presence of NCS seemed to be very important at some crucial stage of the reaction, and the yields of products depended very much on the time of its addition. Thus, formation of **16** (78%) is favored over **15** (10%) by the presence of NCS at the beginning of the reaction, while addition of NCS after 72 h favors **15** (45%) over **16** (25%). When NCS was added in the middle of the refluxing period, yields of products decreased significantly. The yields of the benzo compounds **15** and **16** were much higher than for **7** and **8** from the bicyclic oximes **5** and **6**; combined yields of 70%, 88%, and 95% were obtained depending upon the precise experimental conditions, with isolated yields of up to 45% for **15** and 78% for **16** (Table 2). These reactions were much less sensitive to the quality of the sulfur reagent. Thus, using impure S_2Cl_2 or adding small amounts of SCl_2 to the reaction mixture did not substantially change the reaction yields.

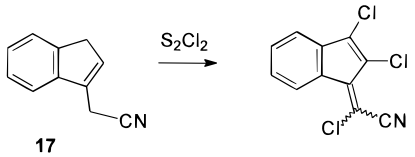
To give support to the structure assigned to product **16** we next studied the reaction of 1-(cyanomethyl)indene (**17**)[16] and S_2Cl_2 under the same conditions. From this reaction we obtained two isomers **18** and **19**, which were also isomeric with, and spectroscopically very similar to, compound **16**, thus supporting its structure. Although close similarities in spectroscopical data did not allow us to assign geometry, calculation of dipoles of **18** and **19** by HyperChem gave a significantly higher value for **18** than for **19**. According to this, it seems reasonable to assign the *E*-structure **18** to the more polar compound and the *Z*-structure **19** to the less polar isomer.[17] Compound **18** showed two phase transitions before melting. Its isomer **19** also showed phase transitions before melting, indicating that liquid crystallinity is a major characteristic of these structures. The reaction affording **18** and **19** involved a sequence of chlorination and dehydrochlorination steps without rearrangement. Al-

(15) Stegmeyer, H. *Liquid Crystals*; Steinkopff: Darmstadt; Springer: New York, 1994; Chapter 1.

(16) Shemyakin, M. M.; Trakhtenberg, D. M. *C. R. Acad. Sci. URSS* **1939**, *24*, 763; *Chem. Abstr.* **1940**, *34*, 3676.

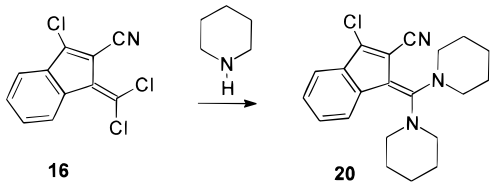
(17) R_f's for **18** and **19** were measured on Merck 60 F_{254} silica TLC precoated plates with petroleum ether−dichloromethane (5:1 v/v) as eluent. R_f for **18** = 0.19; R_f for **19** = 0.34.

though indeno[2,1-*c*]-1,2-dithiole derivatives are known to be stable compounds,[18] they were not detected in these reactions.



17 **18**, **19**

All the products obtained in the oxime−S_2Cl_2 reactions were stable in the presence of acids, but were sensitive to bases. Stirring **16** in dichloromethane with an excess of piperidine at rt afforded only compound **20** (45%), in which two chlorine atoms were substituted by piperidine. A signal at δ 162 in the ^{13}C NMR spectrum of **20**, corresponding to a characteristic $(R_2N)_2C{=}$ moiety,[19] supports the assigned structure.



16 **20**

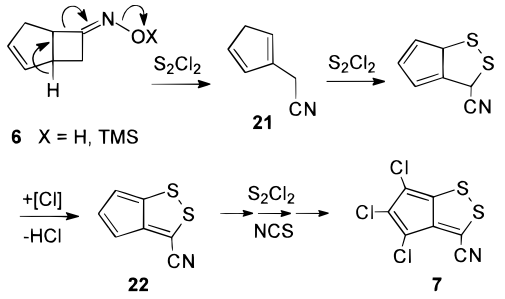
Compound **20** did not show birefringence upon melting between crossed polarizers, showing that molecular interactions between the nitrile and the three chlorine atoms are significant in the liquid crystalline behavior.

Reaction Mechanism

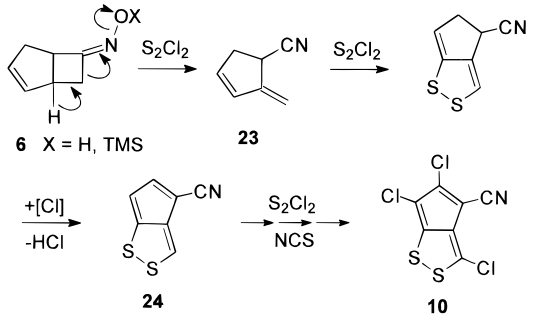
We now propose possible pathways for these reactions and show that a simple, unified set of mechanisms accounts for all the, structurally diverse, products isolated.

The simplest mechanism for the conversion of oximes **5** and **6** into the heteroaromatic products **7**, **8**, and **10** would appear to involve initial ketoxime fragmentation of the abnormal (second-order) Beckmann type,[20] presumably induced by S_2Cl_2 and/or catalyzed by traces of SCl_2. The cyclobutane ring opening processes[21] for the two oxime isomers would give the isomeric nitriles **21**[22] (Scheme 1) and **23** (Scheme 2). The former could react with S_2Cl_2 to give the dithiole ring, which by chlorination and dehydrochlorination could give the unsaturated system **22**, which can be fully chlorinated by S_2Cl_2 and NCS in the carbocyclic ring; all positions of this ring are activated by electron release from the dithiole sulfur atoms, exactly as proposed[6] for the formation of **1** and **2** above. The isomeric nitrile **23** could react with S_2Cl_2 (Scheme 2) to give the isomeric dithiole ring, which by chlorination and dehydrochlorination could give the corresponding unsaturated system **24**, which can be fully

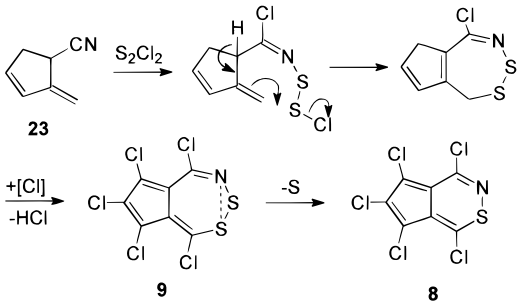
Scheme 1



Scheme 2



Scheme 3



chlorinated by S_2Cl_2 and NCS in the carbocyclic ring, exactly as before. Alternatively, the intermediate nitrile **23** could react by addition of S_2Cl_2 to the nitrile,[23] followed by cyclization as shown (Scheme 3) to give the 7-membered dithiazepine ring, which by the previous dehydrogenation and chlorination sequence would give the fully chlorinated product **9**. This is formally a 12π system that by electrocyclization of the 7-membered ring to a fused 6−3 system followed by loss of sulfur would give the thiazine **8**. The intermediate structure **9** has been isolated as a very minor product that on gentle heating gives compound **8**.

The formation of the two products **15** and **16** from the oximes **14** can be rationalized as shown in Scheme 4. Ring opening of the oximes, as before, gives the key intermediate **24**. This could add S_2Cl_2 to the cyano group to give ultimately product **15**, by exactly the same sequence of reactions as shown in Scheme 3. Alternatively it could directly undergo the chlorination−dehydrochlorination sequence, with S_2Cl_2 and NCS, as demonstrated above for **17** → **18** + **19**, to give product **16**. The relative yields of **15** and **16** depend markedly upon the precise experimental conditions. Thus, the presence of NCS at the beginning of the reaction favors the chlorination of **24** and, hence, formation of **16** (78%) over **15** (10%). Ring opening of the other isomer of oxime **14**, analogous to that shown in Scheme 1, would have given

(18) Hartke, K.; Krampitz, D. *Chem. Ber.* **1974**, *107*, 739.

(19) For calculated and experimental ^{13}C-chemical shifts of $(R_2N)_2C{=}CR'_2$ compounds, see: Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tables of Spectral Data for Structure Determination of Organic Compounds, 2nd ed.;* Springer-Verlag: Berlin, 1989; C95.

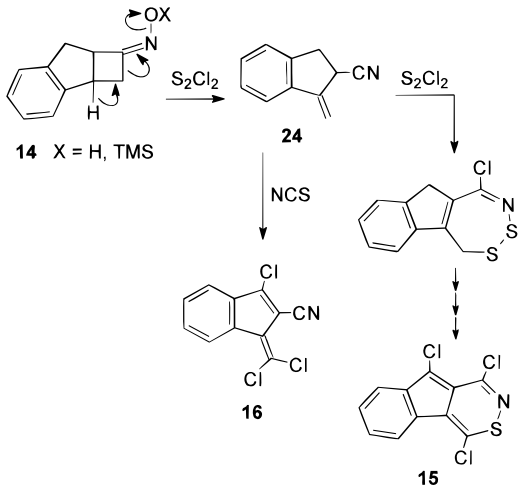
(20) Gawley, R. E. *Org. React. (N.Y.)* **1988**, *35*, 1.

(21) An analogous Beckmann fission of fused cyclobutanone oximes to give cyanomethyl compounds was first demonstrated in 1980: Ikeda, M.; Uno, T.; Homma, K.; Ohno, K.; Tamura, Y. *Synth. Commun.* **1980**, *10*, 437. A few other examples have since been reported: Fráter, G.; Müller, U.; Günther, G. *Tetrahedron Lett.* **1984**, *25*, 1133.

(22) A similar intermediate has been proposed for another Beckmann fragmentation: VerHaeghe, D. G.; Weber, G. S.; Pappalardo, P. A. *Tetrahedron Lett.* **1989**, *30*, 4041.

(23) Martinetz, D. *Z. Chem.* **1980**, *20*, 332.

Scheme 4



compound **17** or the isomer of **17** with the olefinic bond in the alternative ring position. Either of these could have given the products **18** and **19** reported above, but curiously neither were observed in the reactions of oxime **14** with S_2Cl_2.

Conclusions

Several new heterocyclic systems have been formed, in novel molecular rearrangements, in one step from cyclobutanone oximes and a mixture of S_2Cl_2, NCS, and Hünig's base showing that this mixture is valuable for the preparation of heterocycles that are not readily available by other methods. Furthermore, we have demonstrated some control over product formation by the precise experimental conditions, such as the order of addition of the reagents. The cyclopenta-1,2-dithiole, cyclopenta[*d*]-1,2-thiazine products are new members of the pseudoazulene series, and there is clearly scope for extending this synthesis to other pseudoazulenes, as well as new indene derivatives. The study of these products by optical microscopy has revealed unexpected thermal behavior in several of the compounds, which is compatible with the formation of liquid crystal phases, and further evidence is being sought for liquid crystallinity in these and related compounds.

Experimental Section

Disulfur dichloride, sulfur dichloride, NCS, and Hünig's base were purchased from Aldrich. THF was distilled from sodium. Melting points were determined using a Kofler hot stage apparatus and are uncorrected. Column chromatography was carried out on a medium pressure Gilson liquid chromatography apparatus, columns filled with silica gel C60 (Merck). Light petroleum refers to the fraction bp 40−60 °C. Theoretical calculations were carried out using the semiempirical PM3 method on HyperChem version 3. X-ray reflections were measured on a Siemens P4/PC diffractometer with Mo Kα radiation (graphite monochromator) using ω-scans. Computations were carried out on a 486 PC computers using the SHELXTL PC program system version 5.03. Atomic coordinates, bond lengths and angles, and thermal parameters for compounds **7** and **15** have been deposited at the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

General Procedures for the Reaction of Oximes and Disulfur Dichloride: Method A. The corresponding oxime (5 mmol) of *cis*-bicyclo[3.2.0]heptan-6-one (**5**),[9] *cis*-bicyclo[3.2.0]-hept-2-en-6-one (**6**),[9] *cis*-bicyclo[4.2.0]octan-7-one (**12**),[9] *cis*-bicyclo[5.2.0]nonan-8-one (**13**),[14] or 2,3-benzo-*cis*-bicyclo[3.2.0]-heptan-6-one (**14**),[9] and *N*,*N*-diisopropylethylamine (Hünig's base, 6.45 g, 50 mmol) were dissolved in THF (40 mL) and cooled to −50 °C. To the resulting stirred solution were added consecutively disulfur dichloride (4.0 mL, 50 mmol) and a solution of NCS (6.65 g, 50 mmol) in THF (30 mL), and the mixture was stirred at 4 °C for 72 h. Then the mixture was refluxed for 2.5−4.5 h, monitoring the reaction by TLC every 30 min. Then the solvent was removed under reduced pressure and the products were separated by column chromatography (light petroleum and then light petroleum−dichloromethane mixtures).

Method B. Disulfur dichloride (4.0 mL, 50 mmol) was added to a stirred, cold (−50 °C) solution of the corresponding oxime (5 mmol) and *N*,*N*-diisopropylethylamine (6.45 g, 50 mmol) dissolved in THF (40 mL), and the mixture was stirred at 4 °C for 72 h. Then, a solution of NCS (6.65 g, 50 mmol) in THF (30 mL) was added, and the resulting mixture was refluxed for 3.5 h, monitoring the reaction by TLC every 30 min. Then, the solvent was removed under reduced pressure, and the products were separated by column chromatography (light petroleum and then light petroleum−dichloromethane mixtures).

Method C. Trimethylchlorosilane (1.09g, 10 mmol) in THF (10 mL) was added to a solution of the corresponding oxime (5 mmol) and *N*,*N*-diisopropylethylamine (1.29 g, 10 mmol) in THF (10 mL), and the mixture was stirred at room temperature for 1.5 h. Then, *N*,*N*-diisopropylethylamine (6.45 g, 50 mmol) in THF (20 mL) was added and the solution cooled to −50 °C. To the resulting stirred solution were added consecutively disulfur dichloride (4.0 mL, 50 mmol) and a solution of NCS (6.65 g, 50 mmol) in THF (30 mL), and the mixture was stirred at 4 °C for 72 h. Then the mixture was refluxed for 3.5−4 h, monitored, and worked up as in the previous methods. The proportions were modified for method C* as follows: $^{i}Pr_2$-NEt (75 mmol in place of 50 mmol), S_2Cl_2 (75 mmol).

Method D. Trimethylchlorosilane (1.09g, 10 mmol) in THF (10 mL) was added to a solution of the corresponding oxime (5 mmol) and *N*,*N*-diisopropylethylamine (1.29 g, 10 mmol) in THF (10 mL), and the mixture was stirred at rt for 1.5 h. Then, *N*,*N*-diisopropylethylamine (6.45 g, 50 mmol) in THF (20 mL) was added and the solution cooled to −50 °C. Disulfur dichloride (4.0 mL, 50 mmol) was added to the resulting stirred solution, and the mixture was stirred at 4 °C for 72 h. Then, a solution of NCS (6.65 g, 50 mmol) in THF (30 mL) was added, and the mixture was refluxed for 1.5−3 h, monitored, and worked up as in the previous methods. The conditions were slightly modified for method D* as follows: The solution of NCS in THF was added after refluxing of the reaction for 1 h and then refluxed again for 2 h. Then the reaction was worked up as usual.

Method E. 2,3-Benzo-*cis*-bicyclo[3.2.0]heptan-6-one oxime (**14**)[9] (1.04 g, 6 mmol) and phenyl isocyanate (0.72 g, 6 mmol) were stirred in benzene (30 mL) for 1.5 h. Then the solvent was evaporated and the residue crystallized from petroleum ether (1.62 g, 92%). Then method B was followed.

Method F. The corresponding oxime (5 mmol) and *N*,*N*-diisopropylethylamine (6.45 g, 50 mmol) were dissolved in THF (40 mL) and cooled to −50 °C. To the resulting stirred solution were added consecutively a mixture of S_2Cl_2−SCl_2 (obtained by prolonged standing of a sample of S_2Cl_2 or by addition of 5% v/v SCl_2 to a new sample of S_2Cl_2) (4.0 mL, 50 mmol) and a solution of NCS (6.65 g, 50 mmol) in THF (30 mL). Then method A was followed. The conditions for method F* were 10% v/v SCl_2 in S_2Cl_2 as reagent, and the mixture was stirred at 4 °C for 4 days prior to refluxing.

General Procedure for the Reaction of Nitriles and Disulfur Dichloride. 1-(Cyanomethyl)cyclopentene (**11**)[13] or 1-(cyanomethyl)indene (**17**)[16] (5 mmol) and *N*,*N*-diisopropylethylamine (6.45 g, 50 mmol) were dissolved in THF (40 mL) and cooled to −50 °C. To the resulting stirred solution were added consecutively disulfur dichloride (4.0 mL, 50 mmol) and a solution of NCS (6.65 g, 50 mmol) in THF (30 mL). Then method A was followed.

4,5,6-Trichlorocyclopenta-1,2-dithiole-3-carbonitrile (7). Dark blue prisms (from light petroleum-dichloromethane) (0.18 g, 13% from **6**, method C, 0.28g, 20% from **11**). Transition temperatures:

$$\text{crystal} \underset{145\ ^\circ\text{C}}{\overset{178\ ^\circ\text{C}}{\rightleftharpoons}} \text{mesophase} \underset{190\ ^\circ\text{C}}{\overset{190\ ^\circ\text{C}}{\rightleftharpoons}} \text{isotropic liquid}$$

^{13}C NMR (125 MHz, $CDCl_3$) δ: 142.28, 140.42, 131.12, 116.52, 111.38 (intense, C≡N), 109.07, 105.55. IR (CCl_4, cm^{-1}) ν: 2218 (C≡N), 1576, 1532, 1227: UV/vis (DCM) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}): 227 (4.00), 277 (3.82), 376 (4.13), 394 (4.06), 578 (3.11). MS (EI, 70 eV, 180 °C) *m*/*z*: 271 (M^+, 34), 269 (M^+, 100), 267 (M^+, 89), 243 (M − 26, 8), 241 (M − 26, 8), 234 (M − 35, 68), 232 (M − 35, 87), 225 (M − 44, 18), 223 (M − 44, 18). HRMS: M^+ = 266.854 099 $C_7Cl_3NS_2$ requires 266.853 776. Anal. Calcd for $C_7Cl_3NS_2$: C, 31.30; N, 5.21. Found: C, 31.27; N, 5.02.

Crystal Data for 7. $C_7Cl_3NS_2$, M_w = 268.6, hexagonal, a = 15.570(1), c = 6.815(1) Å, V = 1430.7(2) Å^3, space group $P6_3/m$, Z = 6 (the molecule has crystallographic C_s symmetry), D_c = 1.87 g cm^{-3}, μ = 13.4 cm^{-1}, $F(000)$ = 792. A total of 1180 independent reflections ($\theta \leq 27.5°$) were measured with Mo Kα radiation (graphite monochromator) using ω-scans. Of these 1163 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors, but not for absorption. The structure was solved by direct methods, and all the atoms were refined anisotropically. Refinement was by full-matrix least-squares methods based on F^2 to give R_1 = 0.032, wR_2 = 0.084 for 80 parameters.

3,4,5,6,7-Pentachlorocyclopenta[*d*]-1,2-thiazine (8). Orange needles (from light petroleum−dichloromethane) (0.11 g, 7% from **6**, method A*). Transition temperatures:

$$\text{crystal} \xrightarrow{185\ ^\circ\text{C}} \text{mesophase} \xrightarrow{234\ ^\circ\text{C}} \text{isotropic liquid dec}$$

^{13}C NMR (125 MHz, $CDCl_3$) δ: 153.49, 145.57, 134.37, 124.62, 120.14, 113.73, 113.07. IR (CCl_4, cm^{-1}) ν: 1550, 1306, 1258, 1209. MS (EI, 70 eV, 260 °C) *m*/*z*: 311 (M^+, 23), 309 (M^+, 63), 307 (M^+, 100), 305 (M^+, 60), 275 (M − 32, 16), 273 (M − 32, 26), 272 (M − 35, 27), 270 (M − 35, 19), 246 (M − 61, 18), 244 (M − 61, 13), 237 (M − 70, 62), 235 (M − 70, 61); HRMS, M^+ = 306.815 522 $C_7Cl_4{}^{37}ClNS$ requires 306.816 459; M^+ = 304.819 116 C_7Cl_5NS requires 304.819 409; Anal. Calcd for C_7Cl_5NS: C, 27.35; N, 4.56. Found: C, 26.94; N, 4.25.

4,5,6,7,8-Pentachlorocyclopenta[*e*]-1,2,3-dithiazepine (9). Light blue prisms (from light petroleum−dichloromethane) (5 mg, 0.3% from **6**, method F*). Transition temperatures:

$$\text{crystal} \xrightarrow{83\ ^\circ\text{C}} \text{liquid} \xrightarrow{110\ ^\circ\text{C}} \text{orange crystal} \xrightarrow{150\ ^\circ\text{C}} \text{liquid}$$

^{13}C NMR (125 MHz, $CDCl_3$) δ: 154.27, 146.48, 136.21, 126.34, 122.20, 116.52, 114.17. IR (CCl_4, cm^{-1}) ν: 1550, 1322, 1252, 1222, 1125, 1009. MS (EI, 70 eV, 260 °C) *m*/*z*: 311 (M − 32, 23), 309 (M − 32, 63), 307 (M − 32, 100), 305 (M − 32, 60), 275 (M − 64, 16), 273 (M − 64, 26), 272 (M − 67, 27), 270 (M − 67, 19), 246 (M − 93, 18), 244 (M − 93, 13), 237 (M − 102, 62), 235 (M − 102, 61). MS (CI, ammonia): 379 (M + 36, 5), 377, (M + 36, 8), 375, (M + 36, 15), 373, (M + 36, 9).

3,5,6-Trichlorocyclopenta-1,2-dithiole-4-carbonitrile (10). Red powder (0.21g, 15% from **5**, method F), mp 195 °C. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 147.79, 145.45, 138.73, 133.69, 112.45 (intense, CN), 110.95, 87.78. IR (CCl_4, cm^{-1}) ν: 2216 (CN), 1569, 1425, 1331, 1288, 1206. UV/vis (DCM) λ_{max} (log ϵ/dm^3 mol^{-1} cm^{-1}): 204 (4.14), 250 (3.95), 343 (4.02), 355 (3.97), 484 (3.48). MS (EI, 70 eV, 240 °C) *m*/*z*: 271 (M^+, 18), 269 (M^+, 49), 267 (M^+, 47), 236 (M − 35, 17), 234 (M − 35, 74), 232 (M − 35, 100). Linked scan MS (EI): daughters of 267, 232 (M − 35, 100), 197 (M − 70, 5), 188(M − 79, 6); daughters of 232, 197 (32), 190 (79), 188 (100), 105(49); peaks losing fragment 44, 269(4), 267(4), 234(71), 232(100), 198(26); HRMS, M^+ = 266.854 350 $C_7Cl_3NS_2$ requires 266.853 776. Anal. Calcd for $C_7Cl_3NS_2$: C, 31.30; N, 5.21. Found: C, 31.52; N, 4.90.

3,4,9-Trichloroindeno[2,1-*d*]-1,2-thiazine (15). Yellow-orange needles (from light petroleum−dichloromethane) (0.65 g, 45% from **14**, method B). Transition temperatures:

$$\text{crystal} \underset{200\ ^\circ\text{C}}{\overset{215\ ^\circ\text{C}}{\rightleftharpoons}} \text{mesophase} \underset{235\ ^\circ\text{C}}{\overset{240\ ^\circ\text{C}}{\rightleftharpoons}} \text{isotropic liquid}$$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.57 (m, H_a, $J_{a,b}$ = 7.9 Hz, $J_{a,c}$ = 1.1 Hz, $J_{a,d}$ = 0.8 Hz), 7.92 (m, H_d, $J_{c,d}$ = 7.6 Hz, $J_{b,d}$ = 1.0 Hz), 7.73(m, H_b, $J_{b,c}$ = 7.6 Hz), 7.64 (m, H_c). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 145.77, 138.68, 138.45, 129.57 (C−H, from DEPT), 127.50 (C−H, from DEPT), 123.74 (C−H, from DEPT), 120.24 (C−H, from DEPT), 126.58, 117.90. IR (CCl_4, cm^{-1}) ν: 1584, 1560, 1542, 1524, 1295, 1062, 700. MS (EI, 70 eV, 240 °C) *m*/*z*: 291 (M^+, 36), 289 (M^+, 100), 287 (M^+, 99), 252 (M − 35, 7), 226 (M − 61, 10), 219 (M − 70, 11), 217 (M − 70, 77), 210 (M − 79, 29), 208 (M − 79, 43). HRMS, M^+ = 286.911 948 $C_{11}H_4Cl_3NS$ requires 286.913 004. Anal. Calcd for $C_{11}H_4Cl_3NS$: C, 45.78; H, 1.39; N, 4.85. Found: C 45.68; H, 1.30; N, 4.70.

Crystal data for 15: $C_{11}H_4Cl_3NS$, M_w = 288.6, triclinic, a = 7.287(1) Å, b = 9.408(1) Å, c = 9.422(1) Å, α = 113.02(1)°, β = 92.93(1)°, γ = 110.37(1)°, V = 544.0(1) Å^3, space group $P1$, Z = 2, D_c = 1.76 g cm^{-3}, μ = 9.98 cm^{-1}, $F(000)$ = 288. A total of 1806 independent reflections ($\theta \leq 25°$) were measured with Mo Kα radiation (graphite monochromator) using ω-scans. Of these 1630 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz and polarization factors, but not for absorption. The structure was solved by direct methods and was found to be disordered (50:50) about a noncrystallographic C_2 axis lying in the plane of the molecule and approximately coincident with its long axis (see Figure 3). The two half-occupancy molecules were constrained to have the same dimensions, and the C_6 ring geometry was optimized. The positions of the hydrogen atoms were idealized, assigned isotropic thermal parameters, U(H) = 1.2U_{eq}(C) [U(H) = 1.5U_{eq}(CMe)], and allowed to ride on their parent atoms. All of the non-hydrogen atoms were refined anisotropically using full-matrix least-squares methods based on F^2 to give R_1 = 0.032, wR_2 = 0.084 for 290 parameters.

1-(Dichloromethylene)-3-chloroindene-2-carbonitrile (16). Yellow needles (from light petroleum−dichloromethane) (1.0 g, 78% from **14**, method C). Transition temperatures:

$$\text{crystal} \underset{151\ ^\circ\text{C}}{\overset{184\ ^\circ\text{C}}{\rightleftharpoons}} \text{mesophase} \underset{197\ ^\circ\text{C}}{\overset{197\ ^\circ\text{C}}{\rightleftharpoons}} \text{mesophase} \underset{202\ ^\circ\text{C}}{\overset{202\ ^\circ\text{C}}{\rightleftharpoons}} \text{isotropic liquid}$$

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.21 (m, H_a, $J_{a,b}$ = 8.0 Hz, $J_{a,c}$ = 1.2 Hz, $J_{a,d}$ = 0.6 Hz), 7.53 (m, $3H_{b-d}$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 149.71 (d, ^3J = 5 Hz, *C*=CCN), 136.62 (t, ^2J = 9 Hz, *quaternary*C_{arom}), 132.73 (t, ^2J = 9 Hz, *quaternary*-C_{arom}), 132.14 (s), 130.90 (dd, J = 150 Hz, ^2J = 9 Hz, CH, from DEPT), 129.70 (dd, J = 150 Hz, ^2J = 9 Hz, CH, from DEPT), 128.79 (s), 124.72 (dd, J = 205 Hz, ^2J = 7 Hz, CH, from DEPT), 121.51 (dd, J = 204 Hz, ^2J = 9 Hz, CH, from DEPT), 113.62 (s, intense, C≡N), 106.60 (s). IR (CCl_4, cm^{-1}) ν: 2226 (C≡N), 1581, 1522, 707. MS (EI, 70 eV, 220 °C) *m*/*z*: 259 (M^+, 32), 257 (M^+, 96), 255 (M^+, 100), 222 (M − 35, 13), 220 (M − 35, 19), 194 (M − 61, 1), 187 (M − 70, 16), 185 (M − 70, 48), 150 (M − 105, 9). HRMS: M^+ = 254.938 735, $C_{11}H_4Cl_3N$ requires 254.940 932. Anal. Calcd for $C_{11}H_4Cl_3N$: C, 51.50; H, 1.57; N, 5.46. Found: C 50.88; H, 1.63; N, 5.31.

(*E*)-1-(α-Cyano-α-chloromethylene)-2,3-dichloroindene (18). Yellow needles (from light petroleum−dichloromethane) (0.14 g, 11% from **17**). Transition temperatures:

$$\text{crystal} \underset{105\ ^\circ\text{C}}{\overset{110\ ^\circ\text{C}}{\rightleftharpoons}} \text{mesophase} \underset{142\ ^\circ\text{C}}{\overset{142\ ^\circ\text{C}}{\rightleftharpoons}} \text{mesophase} \underset{183\ ^\circ\text{C}}{\overset{183\ ^\circ\text{C}}{\rightleftharpoons}} \text{isotropic liquid}$$

^{1}H NMR (270 MHz, $CDCl_3$) δ: 8.16 (d, $1H_a$, $J_{a,b}$ = 7.0 Hz), 7.40 (m, $3H_{b-d}$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 143.59, 139.00, 137.78, 131.66 (CH, from DEPT), 130.72, 128.63 (CH, from DEPT), 126.38 (CH, from DEPT), 123.67, 119.80 (CH, from DEPT), 113.76 (intense, CN), 103.30. IR (CCl_4, cm^{-1}) ν: 2217

(C≡N), 1603, 1586, 1538, 1448, 763. MS (EI, 70 eV, 200 °C) *m/z*: 259 (M^+, 27), 257 (M^+, 95), 255 (M^+, 100), 223 ($[MH]^+ -$ 35, 44), 222 (M − 35, 30), 221 ($[MH]^+ -$ 35, 73), 220 (M − 35, 40), 194 (M − 61, 1), 187 (M − 70, 20), 186 ($[MH]^+ -$ 70, 26), 185 (M − 70, 74), 151 ($[MH]^+ -$ 105, 25), 150 (M − 105, 18). HRMS, M^+ = 254.939 632, $C_{11}H_4Cl_3N$ requires 254.940 932. Anal. Calcd for $C_{11}H_4Cl_3N$: C, 51.50; H, 1.57; N, 5.46. Found: C 50.08; H, 1.69; N, 5.29.

(*Z*)-1-(α-Cyano-α-chloromethylene)-2,3-dichloroindene (19). Yellow needles (from light petroleum−dichloromethane) (0.25 g, 20% from **17**). Transition temperatures:

$$\text{crystal} \underset{110\ ^\circ\text{C}}{\overset{112\ ^\circ\text{C}}{\rightleftharpoons}} \text{mesophase} \underset{158\ ^\circ\text{C}}{\overset{158\ ^\circ\text{C}}{\rightleftharpoons}} \text{mesophase} \underset{196\ ^\circ\text{C}}{\overset{196\ ^\circ\text{C}}{\rightleftharpoons}} \text{isotropic liquid}$$

^{1}H NMR (270 MHz, $CDCl_3$) δ: 8.20 (d, 1H$_a$, $J_{a,b}$ = 7.7 Hz, $J_{a,c}$ = 0.7 Hz), 7.34 (m, 3H$_{b-d}$). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 142.61, 141.59, 136.86, 131.13 (CH, from DEPT), 129.94, 129.00 (CH, from DEPT), 124.70, 122.82 (CH, from DEPT), 119.68 (CH, from DEPT), 115.14 (intense, CN), 101.75. IR (CCl_4, cm^{-1}) ν: 2221 (C≡N), 1605, 1529, 1451, 766. MS (EI, 70 eV, 200 °C) *m/z*: 259 (M^+, 32), 257 (M^+, 97), 255 (M^+, 100), 223 ($[MH]^+ -$ 35, 19), 222 (M − 35, 23), 221 ($[MH]^+ -$ 35, 31), 220 (M − 35, 28), 194 (M − 61, 2), 187 (M − 70, 18), 185 (M − 70, 47), 150 (M − 105, 10): HRMS: M^+ = 254.941 348 $C_{11}H_4Cl_3N$ requires 254.940 932. Anal. Calcd for $C_{11}H_4Cl_3N$: C, 51.50; H, 1.57; N, 5.46. Found: C 51.29; H, 1.66; N, 5.22.

1-[*Bis*(pentamethyleneamino)methylene)-3-chloroindene-2-carbonitrile (20). Compound **16** (0.5 mmol, 130 mg) was stirred at rt with piperidine (1 mmol, 85 mg) in dichloromethane (15 mL) for 3 h and then worked up. Column chromatography of the residue afforded **20** as a yellow powder (80 mg, 45%), mp 175 °C dec ^{1}H NMR (200 MHz, DMSO-d_6) δ: 7.42 (d, H$_a$, $J_{a,b}$ = 4.0 Hz), 7.27 (d, H$_d$, $J_{c,d}$ = 4.1 Hz), 7.17 (t, H$_b$, $J_{b,c}$ = 3.7 Hz), 7.05 (t, H$_c$), 3.61 (broad, 4H), 3.26 (broad, 4H), 1.79 (broad, 4H), 1.68 (broad, 4H), 1.55 (broad, 4H). ^{13}C NMR (50 MHz, DMSO-d_6) δ: 161.97, 131.39, 129.13, 123.02 (CH, from DEPT), 120.25 (CH, from DEPT), 119.45 (CH, from DEPT), 118.18 (CH, from DEPT), 117.80, 115.09, 99.46, 97.91, 52.01 (broad, CH_2, from DEPT), 50.89 (broad, CH_2, from DEPT), 25.11 (CH_2, from DEPT), 24.53 (CH_2, from DEPT), 23.61 (CH_2, from DEPT). IR (CCl_4, cm^{-1}) ν: 2941, 2203 (CN), 1520, 1447, 1252, 1211, 1091. MS (EI, 70 eV, 230 °C) *m/z*: 355 (M^+, 15), 354 (MH^+, 11), 353 (M^+, 42), 319 (MH − 35, 9), 318 (M − 35, 20), 271 (M − 84, 11), 270 (MH-84, 13), 269 (M − 84, 25). Linked scan MS (EI): daughters of 353, 318 (M − 35, 100), 270 (MH − 84, 19), 269 (M − 84, 19); peaks losing fragment 84, 356 (34), 355 (49), 354 (100), 353 (90), 319 (24), 271 (17). HRMS: M^+ = 353.165 756 $C_{21}H_{24}ClN_3$ requires 353.165 876. Anal. Calcd for $C_{21}H_{24}ClN_3$: C, 71.27; H, 6.84; N, 11.87. Found: C, 71.18; H, 6.78; N, 11.59.

Acknowledgment. We gratefully acknowledge financial support from the *Dirección General de Investigación Científica y Técnica* of Spain (DGICYT Project Nos. PB93-0414 and SAB94-0169), the *Consejería de Educación de la Junta de Extremadura y Fondo Social Europeo* (ref. EIA94−43), the Royal Society, and INTAS (93-624), and we thank the Wolfson Foundation for establishing the Wolfson Center for Organic Chemistry in Medical Science at Imperial College and Dr. B. Ros, Zaragoza University, for her assistance with the liquid crystals.

Supporting Information Available: Photographs (black and white photos are available on microfiche and in the microfilm version; color photos are available electronically) of the liquid crystal mesophases for compounds **7**, **8**, **15**, **16**, **18**, and **19** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information and instructions on accessing the color images.

JO9612234