One-pot synthesis of indeno-1,2-thiazines, -[1,2]dithioles and thiophenes; new liquid crystalline materials

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In a search for further examples of a new type of discotic liquid crystal, we have examined the reactions of S_2Cl_2 in the presence of a chlorinating agent (NCS) and a base (Hünig's base or DABCO), mostly in THF, with cyclopent-1-enylacetic acid **6**, inden-3-ylacetic acid **8** and its nitrile **16** and 1-(dicyanomethylene)indane **22**. The cyclopentene acid **6** gives purple crystals of the trichlorocyclopenta[1,2]dithiole ester **7**, the product of heterocyclic ring formation, chlorination and dehydrochlorination and, unexpectedly, conversion of the acid in THF into its 4-chlorobutyl ester. Indenylacetic acid **8** gives methyleneindenes **10** and **11**, the tricyclic 1,2-dithiolone **12** and the deep purple thiophene **13**. Indenylacetonitrile **16** gives the chlorocyanomethylene indane **17** and the *E*- and *Z*- isomers of both the dichloro-indene **18** and the monochloroindane **19**, depending upon the precise reaction conditions. Dicyanomethylene indane **22** gives the dichloroindene **23** and the red, thermochromic indeno-1,2-thiazine **24**; the analogous cyano-ester **25** gives the corresponding products. On melting, crystals of **13** and **23** are strongly birefringent. Mechanisms are proposed for the new transformations.

Recent searches for useful new materials, which are strongly oriented towards the supramolecular chemistry[1] of heterocyclic compounds, have resulted in some important findings. These include the formation of discotic liquid crystals by molecular self-assembly,[2] and chiral columnar stacks of disk-shaped molecules[3] based on large hydrogen bonded aggregates. The valuable electro-optical effects shown by discotic liquid crystals[4] have stimulated their synthesis and study. During a search for materials with similar electronic and optical properties we discovered a simple route to some heterocyclic pseudoazulenes,[5,6] an entirely new family of discotic liquid crystals,[7] in which the mesophases are supported by intermolecular interactions. In these molecules discotic mesomorphism appears to arise from a balance between the interactions of central aromatic structures with polarised chlorine and sulfur atoms and cyano groups. Neither long aliphatic chains nor hydrogen bonding are necessary to maintain these interactions. We have now continued this investigation based upon the earlier reactions of disulfur dichloride, S_2Cl_2,[5,6] in a search for new structures that retain these novel structural characteristics.

We originally uncovered an extensive transformation of the oximes of simple saturated ketones with S_2Cl_2 into fully unsaturated and chlorinated heteroaromatic systems.[8] Thus cyclopentanone oxime **1** gave the deep violet 10π pseudo-azulene 4,5,6-trichlorocyclopenta-1,2,3-dithiazole **2** with S_2Cl_2 and Hünig's base (EtNPr$^i_2$) in THF at 4 °C; the addition of NCS supplemented the spontaneous chlorination–dehydro-chlorination–chlorination sequence[8] and improved the yield of **2**. In a closely related reaction 1-(cyanomethyl)cyclopentene **3** and S_2Cl_2 under the same conditions gave 4,5,6-trichlorocyclopenta[c][1,2]dithiole-3-carbonitrile **4** as very stable dark blue crystals which showed strong birefringence upon melting in a hot stage polarising microscope.[6] The only other cyclopenta-[1,2]dithiole reported is the thermally stable but air-sensitive 4,6-di-*tert*-butyl derivative.[9]

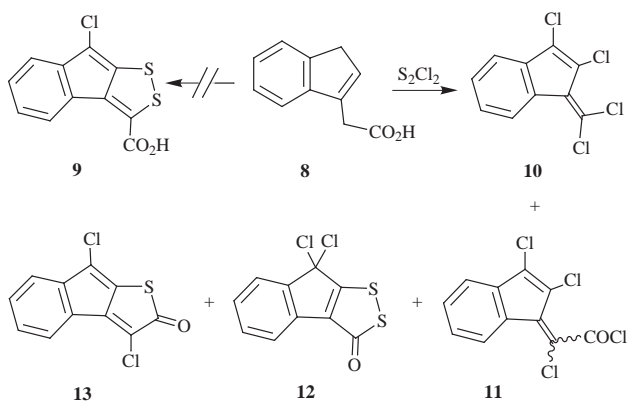In view of the surprising optical properties, and the rarity, of
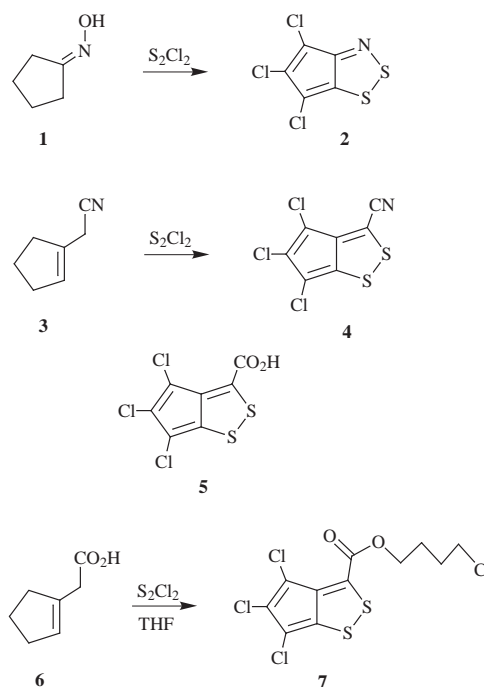
the cyclopenta-1,2,3-dithiazole system we planned to synthesise in a similar manner the carboxylic acid **5**, related to the nitrile **4**, as a key intermediate for other derivatives. When cyclopent-1-enylacetic acid **6** was treated with 10 equivalents each of S_2Cl_2, Hünig's base and NCS in THF at 0 °C for 72 h and then under reflux for 3 h, it gave a modest yield (22%) of a deep purple crystalline product, mp 77–78 °C. Whilst this colour fitted the desired cyclopenta[1,2]dithiole structure **5**, microanalysis, mass spectrometry and NMR showed it to be $C_{11}H_8Cl_4O_2S_2$ with 7 different quaternary carbon atoms and 4 methylene groups, and

the infrared spectrum showed an ester carbonyl group at 1738 cm^{-1}. These data all pointed to the product being the 4-chlorobutyl ester **7** of the expected acid, and this was strongly supported by the mass spectral fragmentation (see Experimental section). The chlorobutoxy group is presumably derived from the THF solvent, possibly by its reaction with the acid chloride derived from acid **5** and S$_2$Cl$_2$ or by initial cleavage of the THF ring by S$_2$Cl$_2$ and subsequent esterification of acid **5**. The formation of acid chlorides by heating carboxylic acids with S$_2$Cl$_2$ has been reported,[10] and THF is known to undergo ring opening with acid chlorides in the presence of iodide ions;[11] we have previously invoked a similar reaction of THF with S$_2$Cl$_2$.[12] The interesting sequence of events leading to the isolated ester **7** is under investigation. Our attempts so far to isolate the free acid **5** from cyclopentenylacetic acid **6** in the absence of THF have failed, possibly because of the sensitivity of **5** to the reagent mixture.

Since the nitrile **3** and the acid **6** had given cyclopentadithioles with S$_2$Cl$_2$ we tuned our attention to the reactions of their benzo derivatives **8** and **16**, both of which proved to be more complex. The analogous products, that is the acid **9** or its 4-chlorobutyl ester, and its nitrile, were not observed although **9** could possibly be an intermediate in the formation of one of the products, the dithiolone **12**.

Inden-3-ylacetic acid **8**[13] was treated with S$_2$Cl$_2$, Hünig's base and NCS in various solvents under a variety of conditions (see Table 1) and chromatography gave four crystalline products (Scheme 1). Two of these did not contain sulfur and were
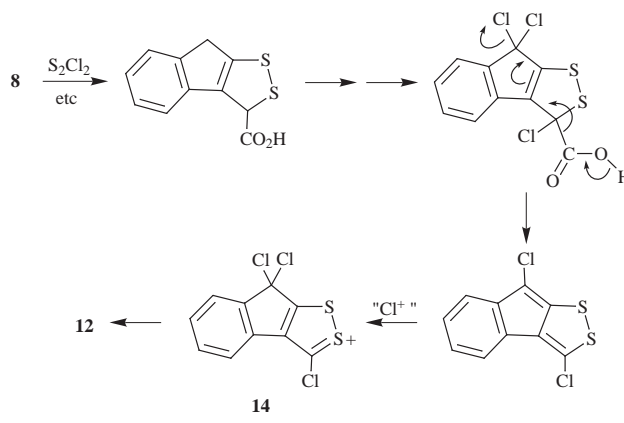
then the mixture heated under reflux for 4.5 h, the dithiole **12** was formed in only 15% yield and the main reaction product was the thiophenone **13**, isolated as deep purple crystals, mp 118–120 °C and then 158–160 °C (37%), accompanied by the methyleneindenes **10** and **11**. Mass spectrometry, HRMS and microanalysis of **13** gave the molecular formula C$_{11}$H$_4$Cl$_2$OS; the ^{1}H NMR spectrum showed only benzo protons, the ^{13}C NMR showed that all the carbon environments were different, and the IR spectrum showed a carbonyl absorption at 1714 cm^{-1}. These data and the colour of the product are in agreement with the extensively delocalized structure, 3,8-dichloroindeno-2H-[2,1-b]thiophen-2-one **13**, which has been confirmed by X-ray crystallography.[16] This structure retains the carbon connectivity of the starting material **8**, now fully unsaturated and substituted, but with the incorporation of only one sulfur atom. Surprisingly, compound **13** showed birefringence on melting in a hot stage polarising microscope, indicating liquid crystalline behaviour, though the dithiole **12** did not.

As can be seen from Table 1 the combined yields of all four products from the indenylacetic acid and S$_2$Cl$_2$ are usually quite high, with a maximum of 85%. Formation of the methyleneindenes **10** and **11** was favoured by THF as solvent, whilst formation of the heterocyclic products **12** and **13** was favoured by chloroform (especially for **12**) and 1,2-dichloroethane.

Whilst the conversion of **8** into the major product **12** was not predicted, a pathway for this can be readily envisaged (Scheme 2) based on the demonstrated propensity for S$_2$Cl$_2$, NCS and

Scheme 1

Scheme 2

shown by their analytical and spectral properties to be polychlorinated methyleneindenes: the yellow tetrachloro compound **10**, obtained in up to 32% yield, and the deep yellow trichloro acid choride **11** (up to 33%). These clearly arose by extensive chlorination and dehydrochlorination of acid **8**, a standard feature of many S$_2$Cl$_2$ reactions,[6,8,14] accompanied by chlorodecarboxylation and acid chloride formation, respectively. The other two products **12** and **13** had incorporated sulfur to form novel and unexpected heterocyclic systems. When the acid **8** was treated with S$_2$Cl$_2$ (9 equiv.), Hünig's base (5 equiv.) in chloroform for three days at 0 °C, followed by the addition of NCS (5 equiv.) and heating of the mixture under reflux for 7 h, the major product (51%) was the yellow crystalline dithiole, mp 99–101 °C, **12**. Mass spectrometry, HRMS and microanalysis gave the molecular formula C$_{10}$H$_4$Cl$_2$OS$_2$ with one less carbon atom than the starting material. The ^{1}H NMR spectrum showed only the benzo protons, the ^{13}C NMR spectrum showed that all the carbon atoms are in different environments, and the IR spectrum showed carbonyl absorption at 1670 cm^{-1}. This suggested 8,8-dichloro-3,8-dihydroindeno[2,1-c][1,2]dithiol-3-one **12** as a possible structure which was confirmed by X-ray crystallography.[15] When the indenylacetic acid **8** was treated with S$_2$Cl$_2$ (10 equiv.), Hünig's base (5 equiv.) and NCS (5 equiv.) in 1,2-dichloroethane for three days at 0 °C and

Hünig's base to form 1,2-dithiole rings with activated allylic systems, followed by extensive chlorination–dehydrochlorination to give fully unsaturated and chlorinated products, as mentioned earlier.[6,8,14] This assumes that the acid group is lost by decarboxylation, possibly to give a 3-chloro-1,2-dithiolium chloride such as **14** which then reacts with some external oxygen nucleophile, as we have proposed in related reactions.[12,14] A possible sequence is outlined in Scheme 2. Formation of the fused thiophenone **13** is, we believe, unprecedented in S$_2$Cl$_2$ reactions. It could arise from a cyclisation reaction of the chloroacid chloride **11** (Scheme 1) with a sulfur nucleophile formed in the reaction mixture from S$_2$Cl$_2$. Alternatively, since S$_2$Cl$_2$ has been shown to convert carboxylic acids into acid chlorides,[10] it is possible that some intermediate in this transformation (such as **15** or its mono-sulfur analogue) could be diverted by cyclisation, ultimately to form **13**. One possibility is outlined in Scheme 3.

Thus the fusion of a benzene ring onto the cyclopentenyl acid **6**, to give **8**, completely changed the course of these S$_2$Cl$_2$ reactions. We decided therefore to investigate the reaction of the benzo analogue **16** of the cyanomethylcyclopentene **3** to see if these changes extended to this more straightforward case where the only product derived from **3** was the dithiole **4**. We expected that the reaction of nitrile **16** would be simpler
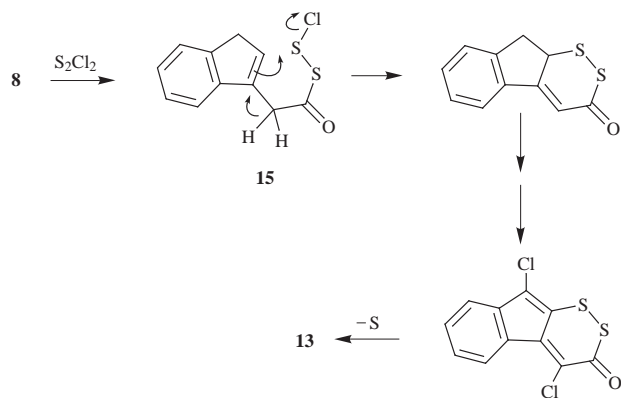
Scheme 3

than that of acid **8** since three of the four products from **8** (*i.e.* **10**, **12**, and **13**, Scheme 1) involved decarboxylation or other transformation of the carboxylic acid group not available to nitrile **16**.

We have already described the conversion of 3-(cyano-methyl)indene **16** with S_2Cl_2 into *E*- and *Z*- isomers of 1-(α-chloro-α-cyanomethylene)-2,3-dichloroindene **18**, both of which show liquid crystalline properties.[6] A more detailed examination of this reaction (Scheme 4, Table 2) has shown
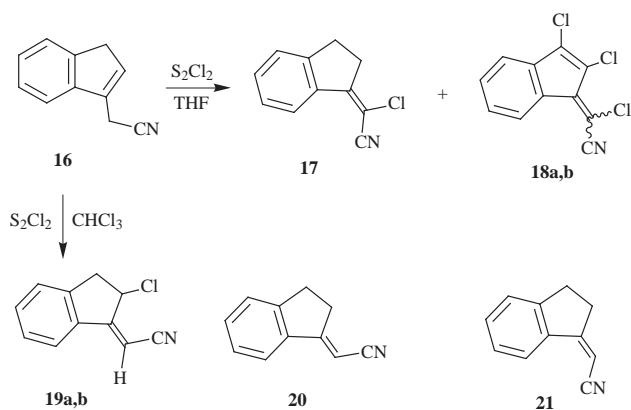
Scheme 4

another product to be *E*-1-(α-chloro-α-cyanomethylene)indane **17** (up to 51%) which is presumably less hindered than the *Z*-isomer. These products derive simply from the chlorination–dehydrochlorination sequence without any incorporation of sulfur. In the hope of favouring heterocyclic ring formation, as with **8**, we repeated the reaction in chloroform but again observed only chlorination to give *E*- and *Z*-isomers of the 2-chloro derivative **19**. For comparison we submitted the 1-(cyanomethylene)indanes **20** and **21** to the standard S_2Cl_2 reaction mixture in THF. The *E*-isomer **20** gave the same products as **16** in almost the same yields, but to our surprise the *Z*-isomer **21** gave no identifiable products under these conditions.

In an attempt to throw more light on these unpredictable reactions we turned to 1-(dicyanomethylene)indane **22** and the analogous cyano ester **25**. The dicyano compound **22** was treated with S_2Cl_2 (9 equiv.), Hünig's base (5 equiv.) and NCS (5 equiv.) in THF at 0 °C for three days and then the mixture was heated under reflux for 5 h. Chromatography afforded orange crystals, mp 133–135 °C and then 163–165 °C, of 1-(dicyanomethylene)-2,3-dichloroindene **23** (70%) and the novel heterocyclic compound **24** as red crystals, mp 206–208 °C (10%) (Scheme 5). The (now expected) unsaturated and chlor-inated structure of **23**, closely analogous to the two isomers **18**, followed from all of its spectroscopic properties. Interestingly it showed birefringence on heating in a hot stage polarising microscope, indicating liquid crystalline behaviour. Mass
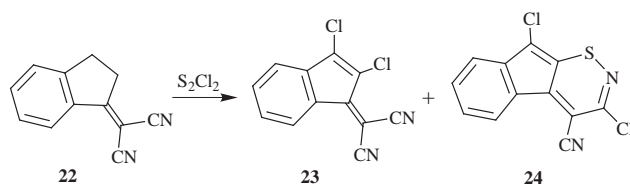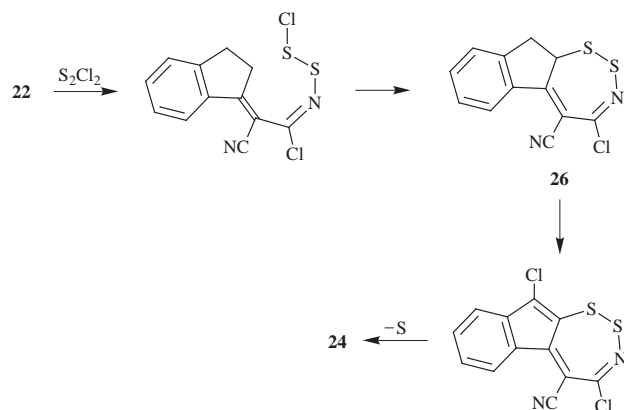

Scheme 5

spectroscopy, HRMS and microanalysis showed the red product to be $C_{12}H_4Cl_2N_2S$; ^{1}H NMR showed only aromatic protons, ^{13}C NMR showed 12 unsaturated carbon signals and the IR spectrum showed a weak nitrile absorption at 2227 cm^{-1}. This all supported the 3,9-dichloroindeno[1,2-*e*]-1,2-thiazine-4-carbonitrile structure **24** which was confirmed by X-ray crystal-lography.[15] Most unexpectedly **24** showed reversible transitions from red to blue crystals on heating and gave a blue melt. It also gave blue solutions in common organic solvents; in DCM its UV spectrum showed λ_{max} 653, ε 946. This is in striking contrast with the yellow-orange cyclopenta- and indeno-1,2-thiazines already reported.[5–7]

When the above treatment of dicyanide **22** was repeated (Table 3) with 5 rather than 9 equivalents of S_2Cl_2 the yield of indene **23** rose to 90% and that of the thiazine **24** hardly changed (9%); in acetonitrile as solvent the yields were very similar, 91% and 6% respectively. Thus the combination of S_2Cl_2, NCS and Hünig's base strongly favours the chlorination–dehydrochlorination product rather than the thiazine **24**. Furthermore, a blank experiment showed that the indene **23** was converted only very slowly into the thiazine **24** under the reaction conditions.

A reasonable pathway for the conversion of dicyanide **22** into thiazine **24** is given in outline in Scheme 6. Addition of S_2Cl_2

Scheme 6

to a nitrile bond[17] followed by cyclisation onto an activated allylic position would give either the dithiazepine **26** or, with loss of sulfur, the thiazine ring directly. Standard chlorination–dehydrochlorination followed by sulfur extrusion (*cf.* ref. 6) would then give the planar and formally aromatic product **24** isolated. The much slower formation of **24** from dichloroindene **23**, with its 2-position being substituted and vinylic, appears reasonable on the basis of this mechanism.

The cyano-ester **25** reacted with S_2Cl_2 in the same way as the dicyano compound **22** to give low yields of the dichloroindenes **27a**–**b** (*Z* and *E* isomers) analogous to **23** and, as a very minor product, the 1,2-thiazine-4-carboxylic ester **28**, analogous to **24** (Scheme 7).

Thus we have shown that a mixture of S_2Cl_2, NCS and EtNPr$^i_2$ or DABCO is very effective for the one-pot conversion of simple cyclopentenes and indenes into a range of highly unsaturated and chlorinated fused carbocyclic and heterocyclic structures. These reactions are somewhat complex, being sensitive to precise experimental conditions and to substrate

Table 1 Reaction of inden-3-ylacetic acid **8** with disulfur dichloride

No.	Reagents/mmol			Solvent	Reflux time/h	Yields (%)			
	EtNPr$^i_2$	S$_2$Cl$_2$	NCS			**10**	**11**	**12**	**13**
1	5	9	5	THF	3	6	33	10	14
2^a	5	9	5	THF	4	19	15	7	11
3^a	10	10	10	THF	4	32	14	15	18
4^a	5	9	5	THF	4	13	24	25	6
5^a	10	10	10	THF	4	4	20	15	6
6	5	9	5	CHCl$_3$	7	6	3	24	8
7	5	10	5	DCE^c	4.5	2	20	15	37
8^b	5	10	5	DCE^c	4.5	9	14	31	31
9^b	5	9	5	CHCl$_3$	7	9	0	51	2

^{a} Tetramethylammonium chloride (10 mg) was added to the reaction mixture. ^{b} NCS was added after 72 h at 0 °C. ^{c} 1,2-Dichloroethane.
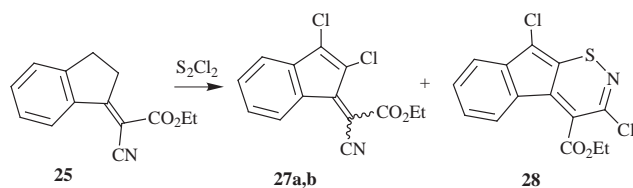
Scheme 7

structure, and are not yet fully understood. However they have succeeded in yielding novel structures, some of which have liquid crystalline properties[18] in spite of the absence of long aliphatic substituents or of extensive H-bonded arrays.

Experimental

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. UV spectrum was recorded on a Perkin-Elmer Lambda 9 instrument in DCM. IR spectra were recorded on a Perkin-Elmer 298 instrument in KBr pellets. ^{1}H NMR spectra were recorded on a Bruker WM 250 spectrometer (250 MHz) and ^{13}C NMR spectra were recorded on a Bruker AM 300 (75.5 MHz) in CDCl$_3$ solution. CH groups were discriminated by DEPT experiments. *J*-values are given in Hz. Mass spectra were recorded on an AEI MS12 instrument using electron impact ionisation. Light petroleum refers to the fraction bp 40–60 °C.

Cyclopent-1-enylacetic acid **6** and inden-3-ylacetic acid **8** were made by literature procedures.

4-Chlorobutyl 4,5,6-trichlorocyclopenta[c][1,2]dithiole-3-carboxylate 7

Disulfur dichloride (4.0 ml, 50 mmol) was added to a stirred solution of the cyclopent-1-enylacetic acid **6** (630 mg, 5 mmol) and *N*-ethyldiisopropylamine (6.45 g, 50 mmol) dissolved in THF (50 ml) at −25 to −30 °C. Then *N*-chlorosuccinimide (6.65 g, 50 mmol) in THF (30 ml) was added and the mixture was stirred at 0 °C for 72 h. Then the mixture was refluxed for 3 h. Solvent was removed under reduced pressure and the residue was separated by column chromatography (silica, light petroleum, and then light petroleum–dichloromethane mixtures) to give **7** (415 mg, 22%) as deep purple crystals, mp 77–78 °C (Found: C, 34.6; H, 2.0. C$_{11}$H$_8$Cl$_4$O$_2$S$_2$ requires C, 34.9; H, 2.1%); δ_H 4.48 (t, 2H, *J* 6.2, CH$_2$), 3.61 (t, 2H, *J* 6.2, CH$_2$), 1.97 (m, 4H, 2CH$_2$); δ_C 158.76, 142.16, 139.40, 135.30, 134.82, 109.29, 105.00, 65.99 (CH$_2$), 44.28 (CH$_2$), 28.90 (CH$_2$), 25.80 (CH$_2$); ν_{max}/cm^{-1} 1738 (C=O), 1567, 1520, 1446, 1239, 1222, 752, 708; *m/z* 376 (M$^+$, 8%), 286 (C$_6$Cl$_3$S$_2$ − CO$_2$H$^+$, 36), 241 (C$_6$Cl$_3$S$_2{}^+$, 15), 207 (C$_6$Cl$_2$S$_2$H$^+$, 17), 171 (C$_6$ClS$_2{}^+$, 6), 136 (C$_6$S$_2{}^+$, 8), 127 (11), 103 (17), 91 (Cl[CH$_2$]$_4{}^+$, 58).

General procedure for the reaction of inden-3-ylacetic acid 8 with disulfur dichloride

Disulfur dichloride was added to a stirred solution of the

inden-3-ylacetic acid **8** (174 mg, 1 mmol) and *N*-ethyldiisopropylamine dissolved in a solvent (20 ml) at −25 to −30 °C. Then *N*-chlorosuccinimide was added and the mixture was stirred at 0 °C for 72 h. Then the mixture was refluxed for the time indicated in Table 1. Solvent was removed under reduced pressure and the products were separated by column chromatography (silica, light petroleum, and then light petroleum–dichloromethane mixtures). The reaction conditions and results are given in Table 1.

1-(Dichloromethylene)-2,3-dichloroindene 10. Light yellow crystals (from hexane), mp 123–125 °C (lit.,[19] mp 125 °C) (Found: M$^+$, 263.9086. C$_{10}$H$_4$Cl$_4$ requires *M*, 263.9067); δ_H 8.15 (d, *J* 7.0, 1H, ArH), 7.30 (m, 3H, ArH); δ_C 113.72 (CCl$_2$), 119.00 (CH), 124.37 (CH), 124.68, 127.56 (CH), 129.12 (CH), 131.69, 131.72, 134.94, 136.96; ν_{max}/cm^{-1} 2920 and 2850 (CH), 1650, 1580, 1440, 1380, 1270, 1160, 1100, 900, 820, 750, 680; *m/z*: 264 (M$^+$, 58%), 229 (M$^+$ − Cl, 4), 194 (M$^+$ − 2Cl, 47), 160 (M$^+$ + 1 − 3Cl, 19), 128 (29), 97 (30).

1-(α-Chloro-α-[chloroformyl]methylene)-2,3-dichloroindene 11. Yellow crystals (from hexane), mp 96–98 °C (Found: M$^+$, 291.8996. C$_{11}$H$_4$Cl$_4$O requires *M*, 291.9016) (Found: C, 45.1; H, 1.3; Cl, 48.0. C$_{11}$H$_4$Cl$_4$O requires C, 44.9; H, 1.4; Cl, 48.2%); δ_H 8.15 (m, 1H, ArH), 7.38 (m, 3H, ArH); δ_C 162.54, 138.22, 136.87, 131.71, 131.23, 130.69 (CH), 128.27 (CH), 126.17, 125.18 (CH), 122.74, 119.79 (CH); ν_{max}/cm^{-1} 1775 (C=O) 1545, 1445, 1200, 1065, 910, 750; *m/z* 292 (M$^+$, 29%), 257 (M$^+$ − Cl, 100), 229 (M$^+$ − COCl, 55), 194 (M$^+$ − COCl$_2$, 81), 159 (M$^+$ − COCl$_3$, 31), 123 (37), 97 (92).

8,8-Dichloro-3,8-dihydroindeno[2,1-c][1,2]dithiol-3-one 12. Yellow crystals (from hexane), mp 99–101 °C (Found: M$^+$, 273.9078. C$_{10}$H$_4$Cl$_2$OS$_2$ requires *M*, 273.9081) (Found: C, 43.8; H, 1.6; Cl, 25.5; S, 23.1. C$_{10}$H$_4$Cl$_2$OS$_2$ requires C, 43.7; H, 1.5; Cl, 25.8; S, 23.3%); δ_H 7.70 (m, 2H, ArH), 7.40 (m, 2H, ArH); δ_C 186.16, 174.19, 150.07, 133.97, 131.85, 131.69 (CH), 129.15 (CH), 125.20 (CH), 120.81 (CH), 78.61 (CCl$_2$); ν_{max}/cm^{-1} 1670 (C=O), 1540, 1480, 1460, 1180, 940, 805, 760, 740; *m/z* 274 (M$^+$, 38%), 239 (M$^+$ − Cl, 11), 210 (M$^+$ − 2S, 100), 176 (M$^+$ − COCl$_2$, 23), 132 (22), 93 (29).

3,8-Dichloroindeno-2H-[2,1-b]thiophen-2-one 13. Deep purple crystals (from hexane), mp 118–120 and then 158–160 °C (Found: M$^+$, 253.9367. C$_{11}$H$_4$Cl$_2$OS requires *M*, 253.9360) (Found: C, 51.5; H, 1.6; Cl, 28.1; S, 12.7. C$_{11}$H$_4$Cl$_2$OS requires C, 51.8; H, 1.6; Cl, 27.8; S, 12.6%); δ_H 7.65 (m, 1H, ArH), 7.25 (m, 3H, ArH); δ_C 188.05, 154.06, 142.71, 133.21, 132.27 (CH), 129.98, 129.37, 128.18 (CH), 125.13, 124.51 (CH), 119.77 (CH); ν_{max}/cm^{-1} 1720 (C=O), 1640, 1560, 1440, 1210, 1120, 900, 800, 760, 750, 700; *m/z* 254 (M$^+$, 100%), 226 (M$^+$ − CO, 59), 191 (M$^+$ − COCl, 22), 156 (M$^+$ − COCl$_2$, 43), 147 (22), 117 (20), 93 (25).

Table 2 Reaction of acetonitrile derivatives **16** and **20** with disulfur dichloride

No.	Starting material	Solvent	T_1/°C	T_2/°C	t_1/h	Yields of products (%)				
						17	**18a**	**18b**	**19a**	**19b**
1	**16**	THF	−25 to −30	0	4	48	2	3.5	0	0
2	**16**	THF	−5 to 0	0	4	51	3	4.5	0	0
3	**16**	CHCl₃	−25 to −30	0	10	5	0	0	60	32
4	**16**	THF + CHCl₃	10 to 12	rt	9	25	0.5	0.5	40	29
5	**20**	THF	−5 to 0	0	4	46	1.5	2	0	0

Table 3 Reaction of dicyanide **22** with disulfur dichloride [a]

No.	S₂Cl₂/ mmol	Solvent	T_3/°C	T_4/°C	t_2/h	Base	Yields (%)	
							23	**24**
1	25	THF	−25 to −35	0	5	DABCO	Low	0
2	45	THF	−5 to 0	0	8	DABCO	10	2
3	25	THF	−25 to −35	0	5	HB	90	9
4 [b]	45	THF	−25 to −35	0	5	HB	70	10
5	45	THF	−5 to 0	0	5	HB	51	7
6	45	THF	15 to 18	rt	6	HB	25	3
7	45	THF	45 to 50	rt	8	HB	35	2
8	45	THF	45 to 50	45 to 55, 2 h	4	HB	19	0
9	45	CH₃CN	−25 to −35	0	5	HB	91	6
10	45	CHCl₃	−25 to −35	0	5	HB	38	5

[a] In the conditions of No. 4 (Table 3, Scheme 7) the cyano-ester **25** gave the analogous *Z*- and *E*-cyano-esters **27a** (26%) and **27b** (10%) respectively and the 1,2-thiazine-4-carboxylic ester **28** (1.5%). [b] NCS was added after 72 h at 0 °C.

The reaction of acetonitrile derivatives 16 and 20 with disulfur dichloride

Disulfur dichloride (4.0 ml, 50 mmol) was added to a stirred solution of the acetonitrile derivative (5 mmol) and *N*-ethyl-diisopropylamine (6.45 g, 50 mmol) dissolved in solvent (50 ml) at T_1 °C. Then *N*-chlorosuccinimide (6.65 g, 50 mmol) in solvent (30 ml) was added and the mixture was stirred at T_2 °C for 72 h. Then the mixture was refluxed for t_1 hours. Solvent was removed under reduced pressure and the products were separated by column chromatography (silica, light petroleum, and then light petroleum–dichloromethane mixtures). The reaction conditions and results are given in Table 2.

E-**1-(α-Chloro-α-cyanomethylene)indane 17.** Light yellow crystals (from hexane), mp 117–118 °C (Found: M⁺, 189.0354. C₁₁H₈ClN requires *M*, 189.0345) (Found: C 69.2; H 4.4; N 7.8; Cl 18.9. C₁₁H₈ClN requires C 69.7; H 4.25; N 7.4; Cl 18.7%); ν_{max}/cm⁻¹ 2210 (CN), 1610, 1590, 1460, 1440, 1410, 1080, 850, 770; δ_H 8.21 (d, *J* 7.9, 1H, ArH), 7.40 (m, 3H, ArH), 3.07 (m, 4H, 2 × CH₂); δ_C 160.40, 150.84, 135.36, 131.66 (CH), 127.37 (CH), 125.76 (CH), 123.86 (CH), 115.75 (CN), 92.21, 33.12 (CH₂), 29.07 (CH₂); *m/z* 189 (M⁺, 50%), 154 (M⁺ − Cl, 100), 127 (M⁺ − CNHCl, 39), 115 (9).

E-**1-(α-Chloro-α-cyanomethylene)-2,3-dichloroindene 18a and *Z*-1-(α-chloro-α-cyanomethylene)-2,3-dichloroindene 18b.** These compounds have been previously described.[6,7]

Z-**2-Chloro-1-(α-cyanomethylene)indane 19a.** Light yellow crystals (from hexane), mp 109–111 °C (Found: M⁺, 189.0354. C₁₁H₈ClN requires *M*, 189.0345) (Found: C 69.6; H 4.4; N 7.3; Cl 18.9. C₁₁H₈ClN requires C 69.7; H 4.25; N 7.4; Cl 18.7%); ν_{max}/cm⁻¹ 2210 (CN), 1620, 1600, 1425, 1340, 1205, 960, 830, 760 (C–Cl); δ_H 7.45 (m, 4H, ArH), 5.70 (s, 1H, C=CH), 5.32 (m, CHCl), 3.70 (m, 1H, CH₂), 3.35 (d, *J* 18.0, 1H, CH₂); δ_C 164.53, 144.94, 135.13, 132.74 (CH), 128.11 (CH), 125.99 (CH), 122.27 (CH), 116.40 (CN), 90.52 (CH), 56.11 (CH), 42.17 (CH₂); *m/z* 189 (M⁺, 49%), 154 (M⁺ − Cl, 100), 127 (M⁺ − HCNCl, 33), 115 (6).

E-**2-Chloro-1-(α-cyanomethylene)indane 19b.** Light yellow liquid, ν_{max}/cm⁻¹ 2220 (CN), 1620, 1600, 1465, 1410, 1300, 1160, 940, 760 (C–Cl); δ_H 8.28 (d, *J* 7.3, 1H, ArH), 7.37 (m, 3H, ArH), 5.65 (s, 1H, C=CH), 5.05 (m, CHCl), 3.60 (m, 1H, CH₂), 3.25 (m, 1H, CH₂); δ_C 162.84, 144.82, 134.47, 132.45 (CH), 125.80 (CH), 124.82 (CH), 118.58 (CH), 116.71 (CN), 90.26 (CH), 58.25 (CH), 41.14 (CH₂); *m/z* 189 (M⁺, 49%), 154 (M⁺ − Cl, 100), 127 (M⁺ − HCNCl, 33), 115 (6).

General procedure for the reaction of dicyanide 22 and disulfur dichloride

Disulfur dichloride (see Table 3) was added to a stirred solution of dicyanide **22** (0.9 g, 5 mmol) and base (DABCO or Hünig's base, 25 mmol) dissolved in solvent (50 ml) at T_3 °C. Then *N*-chlorosuccinimide (3.32 g, 25 mmol) in solvent (30 ml) was added and the mixture was stirred at T_4 °C for 72 h. Then the mixture was refluxed for t_2 hours. Solvent was removed under reduced pressure and the products were separated by column chromatography (silica, light petroleum, and then light petroleum–dichloromethane mixtures). The reaction conditions and results are given in Table 3.

1-(Dicyanomethylene)-2,3-dichloroindene 23. Orange crystals (from hexane), mp 133–135 and then 163–165 °C (Found: M⁺, 245.9806. C₁₂H₄Cl₂N₂ requires *M*, 245.9752) (Found: C 58.3; H 1.75; N 11.4; Cl 28.6. C₁₂H₄Cl₂N₂ requires C 58.3; H 1.6; N 11.3; Cl 28.7%); ν_{max}/cm⁻¹ 2260 (CN), 1470, 1380, 1100, 940, 900; δ_H 8.18 (d, *J* 7.7, 1H, ArH), 7.40 (m, 3H, ArH); δ_C 156.33, 146.05, 137.38, 133.97 (CH), 130.28 (CH), 129.34, 125.14 (CH), 124.53, 120.81 (CH), 112.59 (CN), 110.77 (CN), 79.93 (C=C(CN)₂); *m/z* 246 (M⁺, 100%), 211 (M⁺ − Cl, 23), 176 (M⁺ − 2Cl, 25), 123 (8), 105 (7).

3,9-Dichloro-4-cyanoindeno[1,2-*e*]-1,2-thiazine 24. Red crystals (from hexane), mp 206–208 °C (Found: M⁺, 277.9456. C₁₂H₄Cl₂N₂S requires *M*, 277.9472) (Found: C 51.7; H 1.7; N 9.8. C₁₂H₄Cl₂N₂S requires C 51.8; H 1.4; N 10.1%); λ_{max}/nm 226 (log ε 4.36), 277 (4.43), 299 (4.49), 310 (4.42), 373 (3.78), 653 (2.98); ν_{max}/cm⁻¹ 2227 (CN), 1590, 1530, 1440, 1270, 1240, 1040,

780, 750, 700; δ_H 8.65 (d, J 7.8, 1H, ArH), 7.81 (t, J 7.5, 1H, ArH), 7.50 (m, 2H, ArH); δ_C 147.85, 139.74, 138.64, 134.79 (CH), 126.28, 126.15 (CH), 125.66 (CH), 122.80, 118.15 (CN), 117.62 (CH), 114.00, 101.15; m/z 278 (M$^+$, 100%), 243 (M$^+$ − Cl, 44), 217 (6), 208 (M$^+$ − 2Cl, 25), 199 (20), 164 (7), 138 (8).

Z-1-(α-Cyano-α-ethoxycarbonylmethylene)-2,3-dichloro-indene 27a. Yellow crystals (from hexane), mp 110–111 °C (Found: M$^+$, 292.9965. $C_{14}H_9Cl_2NO_2$ requires M, 293.0010) (Found: C 56.9; H 3.1; N 4.8; Cl 24.5. $C_{14}H_9Cl_2NO_2$ requires C 57.2; H 3.1; N 4.8; Cl 24.1%); v_{max}/cm^{-1} 2210 (CN), 1730 (C=O), 1540, 1450, 1370, 1250, 1200, 1110, 1010, 860, 770, 760; δ_H 8.25 (d, J 8.1, 1H, ArH), 7.35 (m, 3H, ArH), 4.45 (q, J 7.6, 2H, CH$_2$), 1.42 (t, J 7.6, 3H, CH$_3$); δ_C 160.61 (C=O), 147.24, 142.25, 137.64, 132.02 (CH), 130.52, 129.41 (CH), 124.03, 123.95 (CH), 119.99 (CH), 114.70 (CN), 102.83, 63.79 (CH$_2$), 13.84 (CH$_3$); m/z 293 (M$^+$, 23), 258 (M$^+$ − Cl, 12), 248 (15), 230 (M$^+$ − COCl, 100), 220 (16), 185 (56), 174 (15), 150 (40).

E-1-(α-Cyano-α-ethoxycarbonylmethylene)-2,3-dichloro-indene 27b. Yellow crystals (from hexane), mp 98–99 °C (Found: M$^+$, 292.9965. $C_{14}H_9Cl_2NO_2$ requires M, 293.0010) (Found: C 57.1; H 3.2; N 4.85; Cl 24.0. $C_{14}H_9Cl_2NO_2$ requires C 57.2; H 3.1; N 4.8; Cl 24.1%); v_{max}/cm^{-1} 2220 (CN), 1730 (C=O), 1590, 1440, 1360, 1260, 1100, 1080, 765, 750; δ_H 7.68 (d, 1H, J 8.8, ArH), 7.30 (m, 3H, ArH), 4.50 (q, 2H, J 7.5, CH$_2$), 1.45 (t, 3H, J 7.5, CH$_3$); δ_C 161.58 (C=O), 149.38, 142.34, 137.90, 132.17 (CH), 129.86, 128.92 (CH), 125.56 (CH), 119.81 (CH), 113.64 (CN), 104.01, 98.88, 63.82 (CH$_2$), 13.98 (CH$_3$); m/z 293 (M$^+$, 40), 258 (M$^+$ − Cl, 19), 248 (13), 230 (M$^+$ − COCl, 100), 220 (10), 185 (29), 174 (5), 150 (7).

Ethyl 3,9-dichloroindeno[1,2-e]-1,2-thiazine-4-carboxylate 28. Yellow crystals (from hexane), mp 112–113 °C (Found: M$^+$, 324.9746. $C_{14}H_9Cl_2NO_2S$ requires M, 324.9732) (Found: C 51.2; H 2.7; N 4.7. $C_{14}H_9Cl_2NO_2S$ requires C 51.55; H 2.8; N 4.3%); v_{max}/cm^{-1} 1730 (C=O), 1600, 1440, 1280, 1205, 1025, 745; δ_H 7.88 (d, J 8.9, 1H, ArH), 7.70 (t, J 8.1, 1H, ArH), 7.57 (d, J 8.1, 1H, ArH), 7.38 (t, J 8.9, 1H, ArH), 4.65 (q, J 7.4, 2H, CH$_2$), 1.50 (t, J 7.4, 3H, CH$_3$); δ_C 164.45 (C=O), 139.61, 139.23, 137.69, 132.76 (CH), 130.81, 126.57, 124.45 (CH), 124.32 (CH), 122.37, 119.47, 117.23 (CH), 63.37 (CH$_2$), 14.02 (CH$_3$); m/z 325 (M$^+$, 100%), 297 (M$^+$ − CO, 91), 280 (M$^+$ − HCO$_2$, 11), 252 (M$^+$ − CO$_2$C$_2$H$_5$, 5), 217 (31), 206 (13), 182 (13), 138 (20), 109 (4).

Acknowledgements

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