One-pot synthesis of new liquid crystalline indeno heterocyclic materials

Lidia S. Konstantinova,[a] Oleg A. Rakitin,[a] Charles W. Rees,[b] Ljudmila I. Souvorova,[a] Tomás Torroba,[c] Andrew J. P. White[b] and David J. Williams[b]

[a] *N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences, Leninsky Prospect, 47, 117913 Moscow, Russia*
[b] *Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UK SW7 2AY*
[c] *Departamento de Química Orgánica, Facultad de Veterinaria, Universidad de Extremadura, 10071 Cáceres, Spain*

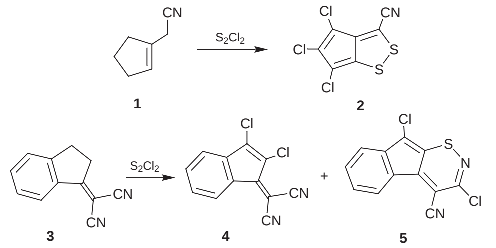
Received (in Liverpool, UK) 8th October 1998, Accepted 18th November 1998

Disulfur dichloride converts 1-(dicyanomethylene)indane 3 into the methyleneindene 4 and the red indeno-1,2-thiazine 5; it also converts inden-3-ylacetic acid 7 into methyleneindenes 8 and 9, dithiolone 10 and the deep purple thiophenone 11; upon melting crystals of 4 and 11 are strongly birefringent and 5 exhibits thermochromicity; mechanisms are outlined for the novel transformations and X-ray crystal structures for 5 and 10 are analysed.

During a search for materials with both novel and useful electronic and optical properties we discovered a simple route to some heterocyclic pseudoazulenes[1] which constitute a new class of discotic liquid crystals where the mesophases are not supported by long aliphatic chains or by H-bonding.[2] The new discotic mesomorphism appears to arise from interactions of central aromatic structures with polarised chlorine, sulfur and cyano groups. In a continuation of this work disulfur dichloride, S_2Cl_2, is shown to react with simple organic substrates to provide new members of this family of molecules which exhibit liquid crystalline behaviour.

We have shown, for example, that S_2Cl_2, NCS and Hünig's base in THF converted 1-(cyanomethyl)cyclopentene **1** into the dark blue trichlorocyclopenta[*c*][1,2]dithiole **2**, crystals of which showed strong birefringence upon melting on a hot stage polarising microscope.[1] We have now selected related indeneacetonitrile and indeneacetic acid derivatives for reaction with the same reagents.

When 1-(dicyanomethylene)indane **3**[3] was treated with 5 equiv. each of S_2Cl_2, Hünig's base and NCS in THF at 0 °C for 3 d and then heated at reflux for 5 h, chromatography gave 2,3-dichloro-1-(dicyanomethylene)indene **4** (90%) as orange crystals, mp 133–135° and then 163–165 °C, and 3,9-dichloroindeno[1,2-*e*][1,2]thiazine **5** (9%) as red crystals, mp 206–208 °C (Scheme 1). The structures of both products followed from their analytical and spectroscopic data and structure **5** was confirmed by X-ray crystallography (Fig. 1).† The ring systems are co-planar to within 0.02 Å with Cl(3) and Cl(9) lying 0.07 and 0.02 Å out of this plane, respectively. The molecules pack to produce slightly distorted close-packed hexagonal sheet arrays, the shortest intermolecular contacts being between the cyano nitrogen atom in one molecule and Cl(3) in a centrosymmetrically related counterpart and *vice versa* (3.18 Å) and between Cl(9) in one molecule and S(1) in the next (3.51 Å) about an independent inversion centre. Adjacent sheets are π-stacked (3.45 Å separation) with the thiazine rings in one sheet overlaying the C_5 rings of another and *vice versa*.



Scheme 1

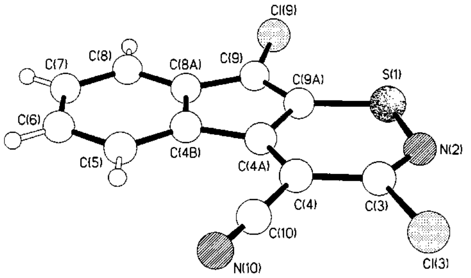
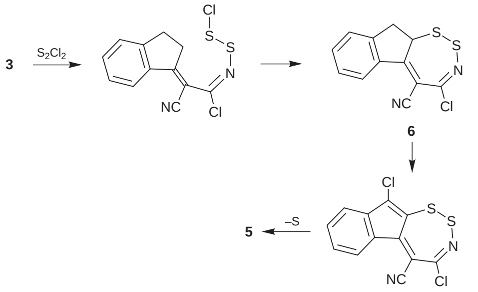


Fig. 1 The molecular structure of **5**.

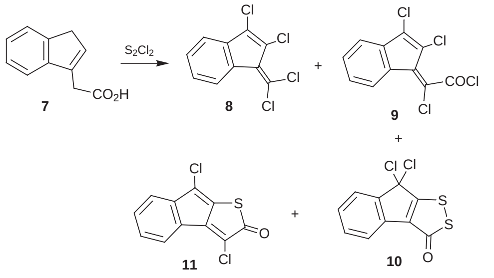
The dichloroindene **4** presumably arises by extensive chlorination and dehydrochlorination, which we have observed in other S_2Cl_2 reactions.[1,4,5] Upon melting on a hot stage polarising microscope, compound **4** exhibited strong birefringence indicative of liquid crystallinity, whilst the indenothiazine **5** showed reversible thermal transitions from red to blue crystals and gave a blue molten phase. Compound **5** also gave blue solutions in common organic solvents, with λ_{max} = 653 nm, ε = 946 in CH_2Cl_2.

A possible pathway, initiated by addition of S_2Cl_2 to a nitrile bond,[6] for the conversion of dicyanide **3** into thiazine **5** is outlined in Scheme 2.



Scheme 2

Inden-3-ylacetic acid **7**[7] was similarly treated with S_2Cl_2, Hünig's base and NCS in THF, $CHCl_3$, or $(CH_2Cl)_2$ to give four products (Scheme 3) in varying yields: the yellow tetra-



Scheme 3

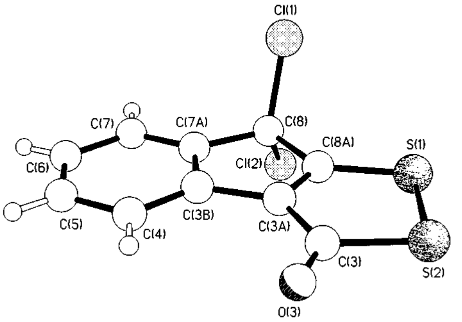


Fig. 2 The molecular structure of **10**.

chloroindene **8**, mp 80–83 °C, in up to 32% yield, the deep yellow acid chloride **9**, mp 96–98 °C (33%) and two unexpected sulfur heterocyclic compounds **10**, mp 97–98 °C (yellow, 51%) and **11**, mp 88–90 °C and then 124–125 °C (deep purple, 37%); combined yields were up to 85%. Structures **8–11** are based on analytical and spectroscopic data, and structure **10** was confirmed as 8,8-dichloro-3,8-dihydroindeno[2,3-*c*][1,2]dithiol-3-one by X-ray crystallography (Fig. 2).† The crystals contain two independent molecules each with very similar geometries, the fused ring systems being co-planar to within 0.09 Å in one and to within 0.04 Å in the other. The out of plane distortions are a consequence of a slight folding (6° in one molecule and 3° in the other) about an axis passing through C(8) and bisecting the C(3A)–C(3B) bond. Pairs of independent molecules are arranged to form essentially co-planar tetrads, interlinked *via* strong O···S interactions[8] [Fig. 3(*a*)–(*d*)] ranging between 2.88 and 3.14 Å. Both the benzo and dithiolo rings are involved in π–π stacking with their symmetry equivalent neighbours.

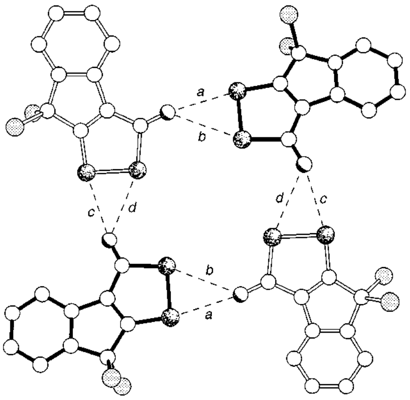
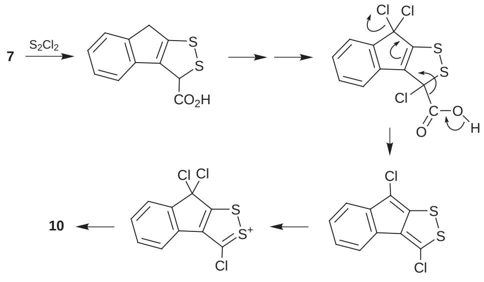


Fig. 3 One of the near co-planar tetrads present in the crystals of **10**. The intermolecular O···S contacts are (*a*) 2.91, (*b*) 3.14, (*c*) 2.88 and (*d*) 3.10 Å. The closed and open bonds serve to distinguish between the two crystallographically independent molecules present in the asymmetric unit.

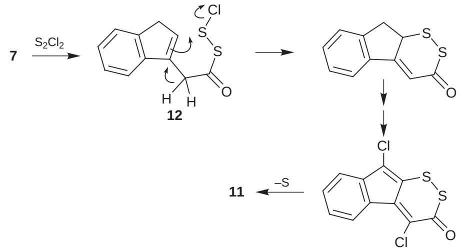
The highly delocalised 3,8-dichloro-2*H*-indeno[2,1-*b*]thiophen-2-one structure **11** is tentatively assigned to the purple product; this retains the carbon connectivity of the starting material **7**, now fully unsaturated and substituted. Encouragingly, compound **11** also showed birefringence on melting on a hot stage polarising microscope.

Routes to the dithiolone **10** and thiophenone **11** from **7** can be envisaged (Schemes 4 and 5). The former is based upon the propensity of the reagents to form 1,2-dithioles with activated allylic substrates, accompanied by extensive chlorination–dehydrochlorination.[4,5,9] The latter, in a new type of S_2Cl_2 reaction, is based on the rare conversion of acids into acid chlorides by S_2Cl_2.[10] An intermediate in this transformation *e.g.* **12**, could be diverted by cyclisation, ultimately to form **11**.

Thus we have shown that some very simple indenes are readily converted by S_2Cl_2 directly into new liquid crystalline and thermochromic materials.



Scheme 4



Scheme 5

We gratefully acknowledge financial support from the Dirección General de Enseñanza Superior of Spain (DGES Project ref. PB96-0101), the Consejería de Educación de la Junta de Extremadura y Fondo Social Europeo (ref. PRI97C123), the Royal Society, the NATO Linkage Grant 970596, an RSC Journals Grant to O. A. R. and the Wolfson Foundation for establishing the Centre for Organic Chemistry in Medical Science at Imperial College.

Notes and references

† *Crystal data* for **5**: $C_{12}H_4N_2SCl_2$, M = 279.1, triclinic, $P\bar{1}$ (no. 2), a = 7.619(1), b = 8.392(2), c = 9.946(2) Å, α = 65.28(1), β = 75.81(1), γ = 84.17(2)°, V = 560.0(2) Å^3, Z = 2, D_c = 1.655 g cm^{-3}, μ(Cu-Kα) = 67.4 cm^{-1}, F(000) = 280. For **10**: $C_{10}H_4OS_2Cl_2$, M = 275.2, triclinic, $P\bar{1}$ (no. 2), a = 8.837(2), b = 10.787(1), c = 12.986(1) Å, α = 68.09(1), β = 75.10(1), γ = 87.02(1)°, V = 1108.4(3) Å^3, Z = 4 (there are two crystallographically independent molecules in the asymmetric unit), D_c = 1.649 g cm^{-3}, μ(Mo-Kα) = 9.27 cm^{-1}, F(000) = 552. 1696 (3819) independent reflections were measured on Siemens P4/PC diffractometers with Cu-Kα (Mo-Kα) radiation using θ–2θ (ω) scans for **5** (**10**) respectively. The structures were solved by direct methods and all of the non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on F^2 with absorption corrected data to give R_1 = 0.039 (0.038), wR_2 = 0.106 (0.090) for 1548 (3143) independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta \leqslant 128°$ (50°)] and 155 (272) parameters for **5** (**10**) respectively. CCDC 182/1098.

1 O. A. Rakitin, C. W. Rees and T. Torroba, *Chem. Commun.*, 1996, 427; O. A. Rakitin, C. W. Rees, D. J. Williams and T. Torroba, *J. Org. Chem.*, 1996, **61**, 9178.
2 J. Barberá, O. A. Rakitin, M. B. Ros and T. Torroba, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 296.
3 D. M. W. Anderson, F. Bell and J. L. Duncan, *J. Chem. Soc.* 1961, 4705.
4 M. J. Plater, C. W. Rees, D. G. Roe and T. Torroba, *J. Chem. Soc., Perkin Trans 1*, 1993, 769.
5 C. W. Rees, A. J. P. White, D. J. Williams, O. A. Rakitin, C. F. Marcos, C. Polo and T. Torroba, *J. Org. Chem.*, 1998, **63**, 2189.
6 D. Martinetz, *Z. Chem.*, 1980, **20**, 332.
7 M. H. Tankard and J. S. Whitehurst, *J. Chem. Soc., Perkin Trans. 1*, 1973, 615.
8 For a recent discussion of such interactions, see Y. Nagao, T. Hirata, S. Goto, S. Sano, A. Kakehi, K. Iizuka and M. Shiro, *J. Am. Chem. Soc.*, 1998, **120**, 3104.
9 C. F. Marcos, C. Polo, O. A. Rakitin, C. W. Rees and T. Torroba, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 281.
10 Y. Takada, T. Matsuda and G. Inoue, *Jap Pat.* 12,123/1968 (*Chem. Abstr.*, 1969, **70**, 19819); A. E. Lippman USP 3,636,102 (*Chem. Abstr.*, 1972, **76**, 72049); T. Matsuda, K. Yokota and Y. Takata, *Hokkaido Daigaku Kogakubu Kenkyu Hokoku*, 1978, **87**, 151 (*Chem. Abstr.*, 1979, **90**, 6055).

Communication 8/07885H