A Thermochromic Reversible [4+4] System

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Summary The deep blue thiones obtained by the photochemical addition of benzo-1,2-dithiole-3-thione to cyclopentene and tetramethylethylene are in thermal equilibrium at ambient temperatures with the corresponding colourless dimers formed by [4+4] addition.

It has been shown that aryl substituted 1,2-dithiole-3-thiones will add photochemically to olefins, the manner of the addition depending on the position of the aryl substituent and the olefin.[1,2] We have now found that the thione (**1**) also gives adducts (80—90% yield) (**2a**) and (**2b**), respectively, with cyclopentene and tetramethylethylene on irradiation.† These adducts, which are deep blue, are in thermal equilibrium with the [4+4] dimers at room temperature. The dimers may be obtained in crystalline form‡ (from CH_2Cl_2–MeOH) but equilibrium is re-established on dissolution.

The structure of the monomer (**2b**) was shown by Diels–Alder addition to *N*-phenylmaleimide and to dimethyl acetylenedicarboxylate to give (**4b**) and (**5**).‡ These were desulphurised with Raney nickel to give (**6**) and (**7**) respectively. The monomer (**2a**) with *N*-phenylmaleimide gave (**4a**), also converted into (**6**).

Our attention to the monomer–dimer equilibrium was drawn, in the case of (**2a**), by the fact that, at *ca.* 10 °C, a 5×10^{-3} M solution in benzene was colourless, but that at *ca.* 50 °C it was deep blue. The apparent molecular weight of (**2a**) in $CHCl_3$ solution (osmometer) was concentration dependent. That the association was dimeric was shown, in the first place, by cryoscopic determination of the molecular weight in benzene (calc.: 504 found: 496 ± 10). Finally, it was shown that $[A]^2/[A_2]$ was constant over the concentration range $2{\cdot}7 \times 10^{-4}$—$5{\cdot}1 \times 10^{-8}$ M, in agreement with the existence of an equilibrium of the type $A_2 \rightleftharpoons 2A$. From the change§ in the value of the equilibrium constant with temperature (16·0—50·6 °C), $\Delta H = 11{\cdot}5 \pm 0{\cdot}4$ kcal mol^{-1} and $\Delta S = 16{\cdot}1 \pm 1{\cdot}4$ cal K^{-1} mol^{-1} were found for (**2a**) in $CHCl_3$. Change to benzene solution favoured dimer formation.

Several structures are possible for the dimers. The Diels–Alder reaction of similar systems with normal dienophiles has been shown,[4] and a similar [2 + 4] addition has

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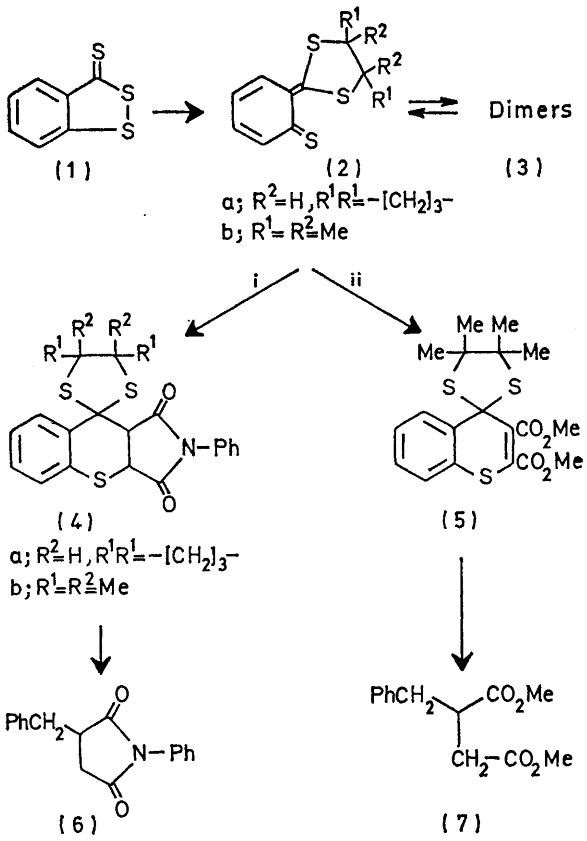
† Et_2O solution under Ni through Pyrex, with a 450 W medium-pressure Hg arc.

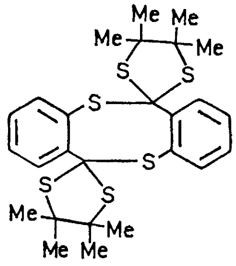
‡ All spectra were in agreement with assigned structures. Adequate analytical data have been obtained for all new compounds [except monomers (**2a**) and (**2b**)].

§ The equilibrium constant was obtained by spectroscopy. The procedure will be described in detail in the full paper, but the technique is based on that of Keussler and Lüttke[3] in their treatment of nitroso-dimer equilibria.



i, *N*-phenylmaleimide; ii, $MeO_2CC{\equiv}CCO_2Me$.

been demonstrated using alicyclic thiones.[5] Such structures, however, could be eliminated because the u.v. absorption of the dimer was essentially below 300 nm. Any [2+4] (or [2+2]) adduct must of necessity leave either an extended conjugated system absorbing above 350 nm, or should contain a spectroscopically recognisable thiocarbonyl group. Adducts of [2+4] type were also excluded by the ^1H (220 MHz) and ^{13}C n.m.r. spectra. These clearly indicated the existence of symmetry, the presence of an aromatic ring with four contiguous hydrogen atoms, and no other unsaturation. Only eight-membered rings remain, *i.e.*, (**8**) and (**9**) in the case of the tetramethyl ethylene derivative. We do not have conclusive evidence to distinguish between (**8**) and (**9**). We have, however, obtained by Raney nickel desulphurisation of the cyclopentene dimer, a small yield (4%) of bibenzyl, which, if no transannular coupling occurs,[6] suggests that (**9**) is correct. Since (**9**) [or (**8**)] shows four methyl ^1H n.m.r. signals (at δ 1·20, 1·33, 1·50, and 1·80), conformational equilibration,



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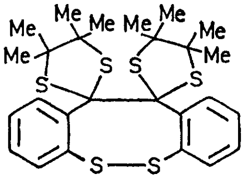

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possible *via* the monomer if not in the dimer itself, must be slow on the n.m.r. time scale at 32°. We have also found that the free energy change in the monomer–dimer interconversion is not the same for the two equilibria and differs by 3·3 kcal mol^{-1} at 20 °C. Since this difference, which is probably steric in origin,¶ is hard to rationalise with a head-to-tail structure for the dimers, we interpret this as additional evidence in favour of structure (**9**).

Added in Proof: We understand from Professor N. Inamoto (Tokyo) that he has made similar observations with cyclopentene, cyclohexane and cyclo-octene adducts and thank him for this information.

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¶ It seems unlikely on chemical grounds, and from a consideration of bond energies, that the two dimers could differ in regiospecificity.

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[2] P. de Mayo and H. Y. Ng, *Tetrahedron Letters*, 1973, 1561.

[3] V. V. Keussler and W. Lüttke, *Z. Elektrochem.*, 1959, **63**, 614; see also R. R. Holmes, *J. Org. Chem.*, 1964, **29**, 3076.

[4] Aside from the data contained in the present communication the trapping of a transient, with a similar chromophore has been reported recently: G. Jacqmin, J. Nasielski, G. Billy, and M. Remy, *Tetrahedron Letters*, 1973, 3655. See also D. B. J. Easton, D. Leaver, and T. J. Rawlings, *J.C.S. Perkin I*, 1972, 41.

[5] P. de Mayo and H. Y. Ng, manuscript in preparation.

[6] O. L. Chapman and C. L. McIntosh, *J. Amer. Chem. Soc.*, 1970, **92**, 7001.