A Stable Dibenzoiodolyl Pyrrolidinedithiocarbamate

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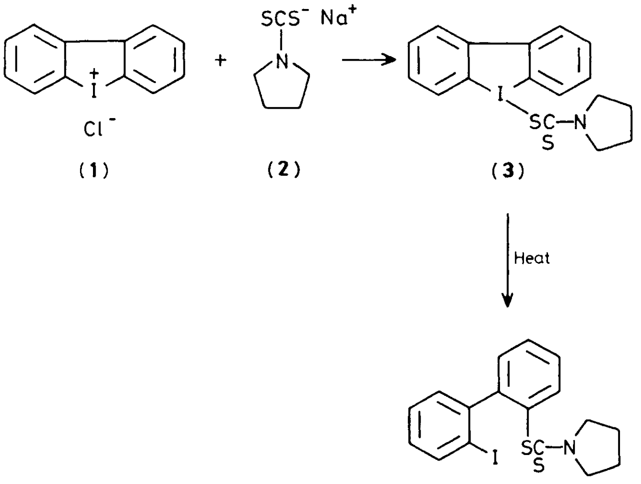
The synthesis and some properties of the title compound are reported; its crystal structure revealed an unusual type of dimer formation and for the first time bond lengths of hypervalent iodine–sulphur have been measured.

Compounds with an iodine–sulphur bond are few and not particularly stable,[1] whereas only one example with hypervalent iodine is known.[2] Considerable recent interest in both compounds of hypervalent iodine[3] and compounds with I–S bonds of various types[4] leads us to report the synthesis, crystal structure, and some properties of dibenzoiodolyl pyrrolidinedithiocarbamate (**3**). By mixing equimolecular quantities of dibenzoiodolium chloride, (**1**) and sodium pyrrolidinedithiocarbamate (**2**), in acetonitrile, a yellow compound [$\lambda_{max.}$ (EtOH) 326 nm, log ε 4.09] was obtained in 61% yield, assigned the iodinane structure (**3**). Compound (**3**) is quite stable; it was recrystallised from chloroform–hexane (m.p. 141—142 °C) and gave a molecular ion in the mass spectrum. Treating (**3**) with hydrochloric acid resulted in the formation of (**1**), whereas thermolysis in boiling *p*-xylene afforded the iodobiphenyl dithiocarbamate ester (**4**), which gave a different mass spectrum from that of (**3**). To ascertain the molecular configuration, a single-crystal *X*-ray analysis of (**3**) was carried out.



(**1**) (**2**) (**3**) (**4**)

Crystal data: $C_{34}H_{32}I_2N_2S_4\cdot2CHCl_3$, M = 1089.46; triclinic, space group $P\bar{1}$, a = 12.082(3), b = 9.859(4), c = 9.638(3) Å; α = 108.46(3), β = 108.29(3), γ = 89.56(3)°; U = 1028.6 Å^3, Z = 1, D_m = 1.765 g cm^{-1}; F(000) = 536, graphite monochromated Mo-K_α radiation, λ = 0.71069 Å, μ(Mo-K_α) = 21.48 cm^{-3}. The diffracted intensities were measured to $2\theta_{max.}$ = 50° on a Philips-PW 1100 four circle diffractometer and were corrected for intensity drop. 1875 Reflections [$I > 2\sigma(I)$] were used to solve the structure by heavy atom methods and difference Fourier techniques. Refinement by full-matrix least-squares with all atoms anisotropic gave R = 0.060 and R_w = 0.055.†

The molecular structure of (**3**), shown along with the most important molecular parameters in Figure 1, is in fact dimeric, as most hypervalent iodine derivatives,[3] but of a novel type. Thus, two molecules related by a centre of symmetry form an 8-membered ring in a chair form. They are connected by two bonds between iodine and sulphur, one 'short intramolecular' and one 'long intermolecular,' in contrast to the more symmetrical bonds of iodine–halogen in diphenyl-iodonium

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

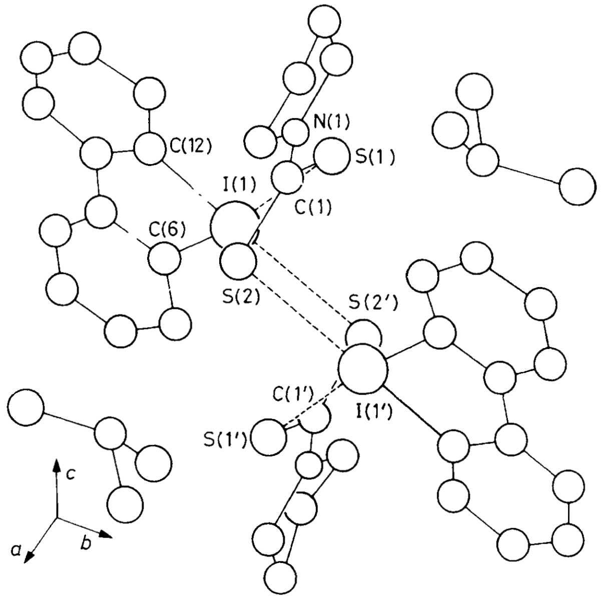

Figure 1. The molecular structure of $C_{34}H_{32}I_2N_2S_4{\cdot}2CHCl_3$ (clinographic projection). Bond lengths: I(1)–S(1), 3.053(4); I(1)–S(2), 3.893(4); I(1)–S(2′), 3.162(4); I(1)–C(6), 2.13(1); I(1)–C(12), 2.11(2); C(1)–S(1), 1.71(2); C(1)–S(2), 1.73(2); C(1)–N(1), 1.31(2) Å. Bond angles: S(1)–I(1)–S(2′), 94.5(1); S(1)–I(1)–C(6), 172.5(5); S(1)–I(1)–C(12), 91.9(3); S(2′)–I(1)–C(6), 91.1(4); S(2′)–I(1)–C(12), 169.8(4); I(1)–S(1)–C(1), 104.3(4); I(1′)–S(2)–C(1), 96.1(5); C(6)–I(1)–C(12), 81.9(5)°.

halides.[5] The lengths of these bonds (3.053 and 3.162 Å, respectively) are much longer than the sum of the covalent radii (2.37 Å), so that they can be regarded as of approximately 0.5 bond order. They actually fall within the range of charge-transfer complexes.[4a] There is also a third I–S bond (3.893 Å) close to the sum of the van der Waals radii (4.00 Å). The co-ordination of iodine is planar tetragonal and the system C–I–S almost linear, so that (**3**) may be described as essentially ionic with two strong secondary bonds.[6,7] The dithiocarbamate moiety shows strong double bond character between N(1) and C(1) whose distance is only 1.31 Å.

The marked biocidal properties of iodonium and dithiocarbamate salts suggest that (**3**) might be more active than either species individually.

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