Reactions of tosyl azide with 2-phenoxy- and 2-phenylsulfanyl-2,3-dihydro-1*H*-indane-1,3-dione. Unexpected reactivity of intermediate 4-acyl-5-hydroxy-1-tosyltriazolines

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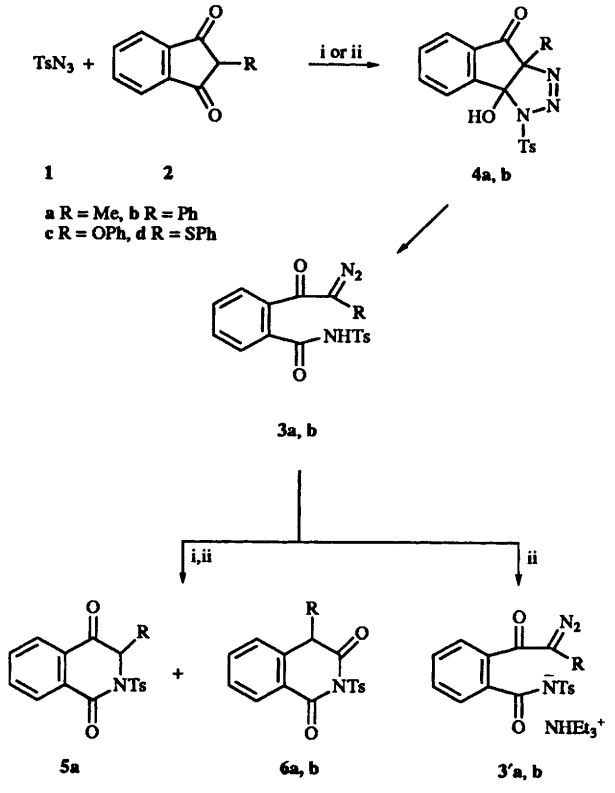
The reaction of tosyl azide **1** with 2-phenoxy-2,3-dihydro-1*H*-indane-1,3-dione **2c**, carried out in hexamethylphosphoramide (HMPA) or in diethyl ether in the presence of triethylamine, fails to afford the expected diazo transfer product, *i.e.* the diazoacetophenone **3c** (**3c'**), but instead leads to the dimeric indanedione **7** the formation of which is primarily ascribable to preferential fragmentation of the transient hydroxytriazoline **4c** to give zwitterion **9c** and dinitrogen. Under comparable conditions, tosyl azide **1** and 2-phenylsulfanyl-2,3-dihydro-1*H*-indane-1,3-dione **2d** in HMPA gives the ring-expanded hydroxybenzopyran **15**, the formation of which is similarly ascribed to preferential fragmentation of the corresponding 4,5-dihydro-1*H*-triazole **4d** to give zwitterion **9d**. However, analogous reaction of the dione **2d** in THF, in the presence of triethylamine, affords 2-diazo-2,3-dihydro-1*H*-indane-1,3-dione along with diphenyl disulfide, toluene-*p*-sulfonamide and phenyl toluene-4-thiosulfonate. These latter products are believed to arise from ready decomposition of the 4,5-dihydro-1*H*-triazole **4d** precursor, *i.e.* the triazenyl anion **13**. X-Ray crystal structure analyses of compound **7** and the acetoxybenzopyran **17** are also reported.

In previous work[1,2] we studied the reaction of toluene-4-sulfonyl (tosyl) azide **1** with 2-methyl- **2a** and 2-phenyl-2,3-dihydro-1*H*-indane-1,3-dione **2b** as a route to the synthetically useful *o*-*N*-tosylcarbamoyl-substituted α-diazoacetophenones **3a**, **b** which might arise from ring-cleavage isomerization of the reactive 5-hydroxy-1-tosyl-4,5-dihydro-1*H*-triazole adducts **4a**, **b** initially produced. In neat hexamethylphosphoramide (HMPA), at room temperature, the azide **1** with the indanedione **2a** gave an isomeric 1:1 mixture of the 2-tosylisoquinolinediones **5a** and **6a**, the formation of which is ascribable to decomposition of the transient diazo compound **3a** (Scheme 1),[1] whereas with the indanedione **2b** led to the isoquinolinedione **6b**, the formation of which is similarly ascribable to the decomposition of the corresponding diazocarbonyl compound **3b** (Scheme 1).[1]

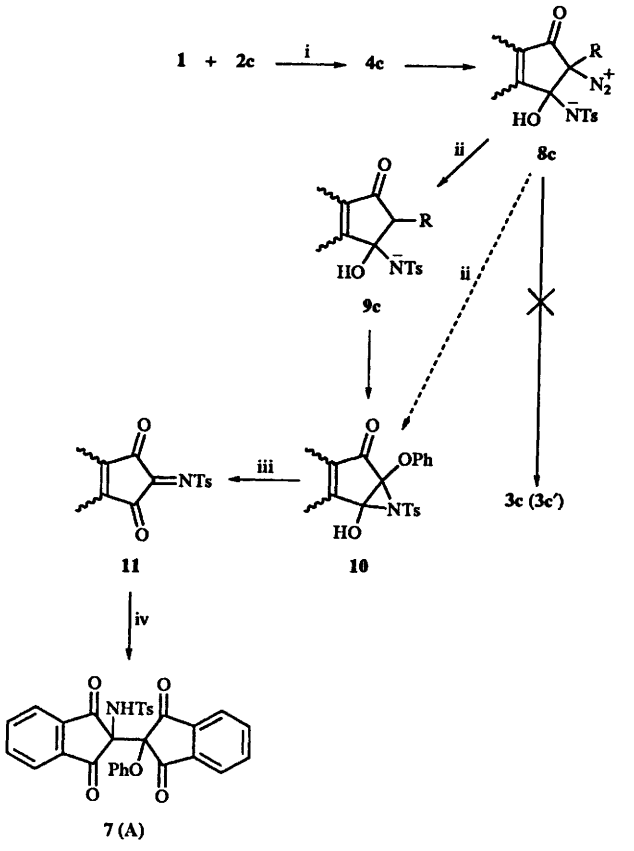
However, both diazoacetophenones **3a**, **b** could be isolated, as their triethylamine salts **3'a**, **b**, when the reaction of the tosyl azide **1** with the diones **2a**, **b** was performed in diethyl ether or THF in the presence of triethylamine (Scheme 1).[2] In order to ascertain the scope of our diazo transfer reaction we examined the reactivity of 2-phenoxy- **2c** and 2-phenylsulfanyl-2,3-dihydro-1*H*-indane-1,3-dione **2d** with tosyl azide **1**. We now present the results obtained which reveal the unexpected failure of these latter indanediones **2c**, **d** to afford the corresponding diazo transfer products **3c**, **d** (or **3'c**, **d**).



Scheme 1 *Reagents and conditions:* i, HMPA, 25 °C; ii, diethyl ether or THF, Et_3N; iii, $-N_2$

Results and discussion

In HMPA, at room temperature, the previously known 2-phenoxy-2,3-dihydro-1*H*-indane-1,3-dione **2c**[3] underwent smooth reaction with tosyl azide **1** (1 equiv.), resulting in the evolution of molecular nitrogen with concomitant formation of a solid compound **A** which was isolated in good yield. The same compound **A** was similarly obtained in comparable yield when the dione **2c** was treated with the azide **1** (3 equiv.) in diethyl ether in the presence of 1 equiv. of triethylamine.[2] In neither case was any evidence provided for the occurrence of diazocarbonyl product **3c** (**3c'**). The IR spectrum of the isolated compound **A** exhibited one NH stretching band at 3340 cm^{-1} and two carbonyl bands at 1760 and 1720 cm^{-1}. Its ^1H NMR spectrum, in addition to a singlet methyl resonance at δ 2.40 and an amino proton resonance at δ 6.60, showed 17 protons in the aromatic region. Elemental analysis suggested a molecular formula of $C_{31}H_{21}NO_7S$. This was however not supported by its mass



Scheme 2 *Reagents and conditions:* i, HMPA or diethyl ether, Et_3N; ii, $-N_2$; iii, $-PhOH$; iv, $+$**2c**

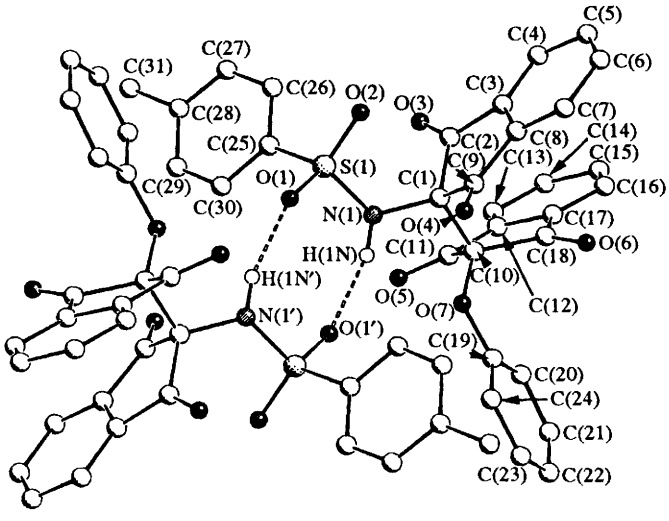


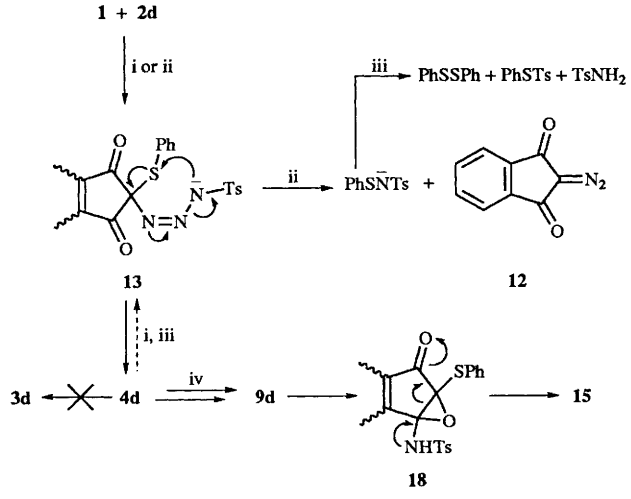
Fig. 1 SCHAKAL perspective view of the molecular structure of the two dimeric indanedione **7** units linked through a double hydrogen bond; the labelling scheme is reported and primed atoms refer to a translation $1 - x, -y, 1 - z$. Hydrogen atoms, with the exception of H(1N), are omitted for clarity.

spectrum which showed no molecular ion, but abundant fragmentation ions at *m/z* 381 ($C_{24}H_{13}O_5$), 238 ($C_{15}H_{10}O_3$) and 158 ($C_9H_4NO_2$). Subsequent X-ray crystal structure analysis unambiguously proved that compound **A** was actually the dimeric indanedione **7** (Scheme 2 and Fig. 1).

The formation of product **7** can be explained in terms of the mechanism depicted in Scheme 2, entailing primary intervention of the transient triazoline **4c**, analogous to those postulated for the corresponding reactions of the diones **2a**, **b** with the azide **1**. In a similar manner to its congeners **4a**, **b**, the triazoline **4c** would suffer heterolytic ring opening to give diazonium betaine **8c**. However, betaine **8c**, unlike its analogues **8a**, **b**, preferentially undergoes extrusion of nitrogen to form the zwitterion **9c** rather than carbon–carbon fission to form the diazo product **3c**. This behaviour is a consequence of the greater ability of the phenoxy group than the methyl and phenyl substituents to confer stabilization on the adjacent positively charged carbon of the zwitterion **9** rather than on the adjacent (negative) carbon of the diazo compound **3**.

The ensuing zwitterion **9c** then leads to indanedione **11** through rearrangement, with elimination of (detected) phenol, of the intermediate aziridine **10**. Further reaction of compound **11** with the unchanged dione **2c** would eventually afford the observed product **7**. A decomposition mode similar to that suggested for the postulated triazoline **4c** was previously encountered in the acid-induced fragmentation of related methyl-substituted 5-hydroxy-1-aryltriazolines **4a** (Ts = Ar) leading to 2-arylamino-2-methylindanediones.[1]

In a similar manner to the dione **2c**, 2-phenylsulfanyl-2,3-dihydro-1*H*-indane-1,3-dione **2d** also failed to afford the respective diazocarbonyl compound **3d** (**3d'**) from its reaction with tosyl azide **1**. However, the product pattern exhibited by this latter reaction was found to be entirely different and totally dependent upon the experimental conditions employed. The dione **2d** had been previously prepared in low yield by a somewhat tedious procedure using ethyl 2-bromo-1,3-dioxoindane-2-carboxylate as the starting material.[4] In the present work the compound **2d** was readily produced in excellent yield by direct sulfenylation of the parent indanedione with *N*-methyl-4'-nitrobenzenesulfenanilide.[5] In diethyl ether, in the presence of triethylamine (1 equiv.), 2-phenylsulfanyl-2,3-dihydro-1*H*-indane-1,3-dione **2d** was converted into its insoluble triethylamine salt which was totally unreactive towards the tosyl azide **1**. However, in THF at 50 °C, this salt slowly reacted with a three-fold excess of the azide **1** to give a rather complex mixture from which 2-diazo-2,3-dihydro-1*H*-indane-1,3-dione **12** (36%), diphenyl disulfide (PhSSPh) (77%), phenyl toluene-4-thiosulfonate (PhSTs) (22%), and toluene-*p*-sulfonamide ($TsNH_2$) (40%) could be isolated as the only identifiable products (Scheme 3). In this case the initially-formed triazenyl

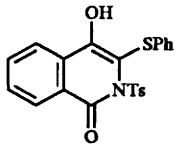


Scheme 3 *Reagents and conditions:* i, HMPA, 25 °C; ii, THF, Et_3N, 50 °C; iii, $+H^+$; iv, $-N_2$

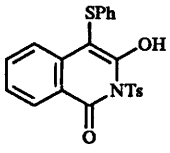
anion **13**[1,6] rather than its cyclized triazoline **4d** would be primarily involved in the product formation. Preferred fragmentation of the anion **13**, in fact, might conceivably afford 2-diazo-2,3-dihydro-1*H*-indane-1,3-dione **12** and benzenesulfenamido anion ($PhSNTs^-$) and the further reaction of the latter might furnish PhSSPh, PhSTs and $TsNH_2$ (Scheme 3).

This possibility was clearly supported by our observation that under similar conditions *N*-tosylbenzenesulfenamide (PhSNHTs) decomposed to give PhSSPh, PhSTs and $TsNH_2$.

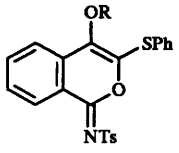
In contrast to the reaction in THF, in HMPA the dione **2d** smoothly reacted at room temperature with 1 equiv. of the azide **1** to give mainly a single compound **B**, which had the molecular formula $C_{22}H_{17}NO_4S_2$ according to elemental analysis and mass spectral evidence. The IR spectrum of this compound **B** showed one OH stretching band at 3445 cm^{-1} and one fairly strong band at *ca.* 1570 cm^{-1}. Its ^1H NMR spectrum showed a singlet methyl resonance at δ 2.3, a singlet hydroxy resonance at δ 5.85 and 13 proton resonances in the aromatic region. Its ^{13}C NMR spectrum revealed besides aromatic CH carbons, seven quaternary carbons in the vinylic/aromatic region along with one amide-carbonyl/imino-ester-imino carbon at δ 159. Overall spectral and analytical data did not allow a definite assignment of compound **B**, but they strongly suggested that it has a hydroxyquinoline **14** (or **14′**) or hydroxybenzopyran **15** (or **15′**) structure.



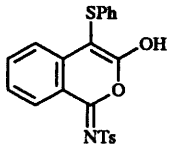
14



14′



15 R = H
16 R = Me
17 R = Ac



15′

Upon treatment with diazomethane at room temperature compound **B** was totally converted into its methoxy derivative, and in refluxing acetic anhydride it was smoothly transformed into its acetoxy derivative. The structure of this latter derivative was established by X-ray crystallographic analysis which proved it to be the acetoxybenzopyran **17** (Fig. 2). Consequently, the original compound **B** was proved to be the hydroxybenzopyran **15** and its methoxy derivative the methoxybenzopyran **16**.

Formation of the ring-expanded benzopyran **15** suggests that in HMPA the azide **1** reacts with the dione **2d** to give the transient hydroxytriazoline **4d**. Heterolytic ring opening of **4d**, in a similar manner to the phenoxy derivative **4c**, would afford the zwitterionic intermediate **9d**. This intermediate **9d** then leads to the benzopyran **15** through ring-cleavage rearrangement of the initially formed oxirane **18** (Scheme 3). In principle, isomerization of **4d** to diazo keto amide **3d** and subsequent intramolecular cyclization of the latter might represent an alternative route to the benzopyran **15**. However, it would be unreasonable to expect that the diazo compound **3d**, in sharp contrast with its methyl and phenyl analogues **3a**, **b**, would not undergo Wolff-type rearrangement (to give eventually **15′** and/or **14′**), and just only intramolecular nucleophilic displacement of dinitrogen by the oxygen rather than nitrogen atom of the adjacent carbamoyl substituent would take place.

In conclusion, we have discovered that our deacylating diazo transfer reaction fails with 2-phenoxy- **2c** and 2-phenylsulfanyl-2,3-dihydro-1*H*-indane-1,3-dione **2d**. These types of oxygen and sulfur substituents would discourage isomerization of the intermediate triazoline **4** to the diazo keto amide **3** in favour of its decomposition to zwitterion **9** as a consequence of effective resonance stabilization on the ensuing zwitterion **9** positive

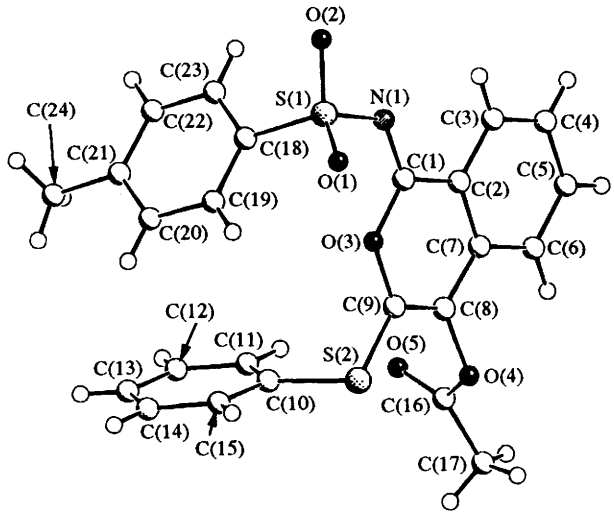


Fig. 2 SCHAKAL perspective view of the molecular structure of the acetoxybenzopyran **17** showing the numbering scheme

centre. At this stage it would be of interest to compare the possible chemical behaviour of other similarly substituted cyclic and acyclic 1,3-diones towards tosyl azide **1**, but to our knowledge chemical evidence in this respect is to date lacking. Studies are in progress in this direction.

Experimental

Tosyl azide **1** [7] and *N*-tosylbenzenesulfenamide [8] were prepared according to literature methods. Known reaction products such as diphenyl disulfide, toluene-*p*-sulfonamide, phenyl toluene-4-thiosulfonate [9] and 2-diazo-2,3-dihydro-1*H*-indane-1,3-dione **12** [10] were identified by spectral comparison with authentic specimens commercially available or independently prepared. All mps (Kofler melting point apparatus) are uncorrected. ^1H and ^{13}C NMR spectra were performed in $CDCl_3$ with Me_4Si as internal standard and recorded on a Varian Gemini 200 spectrometer. IR spectra were performed in $CHCl_3$ and recorded on a Perkin-Elmer 257 spectrometer. Mass spectra were determined by the electron impact method (70 eV) on a VG 7070 instrument. Column chromatography was carried out on ICN silica gel 63–200 60A by gradual elution with light petroleum (bp 40–70 °C)–diethyl ether and final elution with dichloromethane.

Preparation of 2-phenoxy-2,3-dihydro-1*H*-indane-1,3-dione 2c

This was basically accomplished according to the procedure described by Furdik *et al.*[3] The indanedione **2c** had mp 118–120 °C ($CHCl_3$) (lit.,[3a] mp 90–91 °C); δ_H 5.28 (1 H, s), 7.0–7.22 (3 H, m), 7.22–7.33 (2 H, m) and 7.92–8.0 (4 H, m); *m/z* 238.0626 (M^+, 100%. $C_{15}H_{10}O_3$ requires *M*, 238.0630), 149, 133, 104 and 77 (Found: C, 75.45; H, 4.2. $C_{15}H_{10}O_3$ requires: C, 75.6; H, 4.25%).

Preparation of 2-phenylsulfanyl-2,3-dihydro-1*H*-indane-1,3-dione 2d

A solution of *N*-methyl-4′-nitrobenzenesulfenanilide [5] (4 mmol) and (commercially available) indane-1,3-dione (4 mmol) in anhydrous acetonitrile (20 cm^3) was rapidly treated with sodium hydride (4 mmol) and then stirred at room temperature for 20 h. After this time diethyl ether (50 cm^3) was added to the reaction mixture and the ensuing precipitate was filtered off and dissolved in water (*ca.* 20 cm^3). Acidification with concentrated hydrochloric acid, extraction with diethyl ether and final removal of the diethyl ether gave the title compound (3.40 mmol, 85%) as a yellow solid, mp 86–88 °C (lit.,[4] mp 92 °C); δ_H 4.15

(1 H, s), 7.10–7.25 (3 H, m), 7.4–7.6 (2 H, m) and 7.75–8.0 (4 H, m); *m/z* 254.0386 (M^+. $C_{15}H_{10}O_2S$ requires *M*, 254.0401), 132, 109 and 104.

Reaction of tosyl azide 1 with 2-phenoxy-2,3-dihydro-1*H*-indane-1,3-dione 2c

A stirred solution of the dione **2c** (2 mmol) in HMPA (1 cm^3) (**CAUTION**: HMPA is highly toxic and suspected of being a carcinogen) was treated with tosyl azide **1** (2 mmol), at room temperature. Fairly rapid evolution of dinitrogen was observed with concomitant formation of a pale yellow precipitate. After being stirred for *ca.* 3 h the reaction mixture was treated with diethyl ether (20 cm^3) and the precipitated solid material was filtered off to give, after column chromatography (40 : 60 ethyl acetate–light petroleum) *2-phenoxy-2′-tosylamino-2,2′,3,3′-tetrahydro-*1H,1′H-2,2′-*biindane*-1,3-*dione* **7** (0.7 mmol, 70%), mp 236–238 °C; ν_{max}/cm^{-1} 3340 (NH), 1760 (C=O) and 1720 (C=O); δ_H 2.40 (3 H, s), 6.60 (1 H, s, removed upon D_2O shaking), 6.75–6.80 (2 H, m), 6.85–7.08 (3 H, m), 7.28 (2 H, d, *J* 8.6) and 7.65–7.8 (10 H, m); *m/z* 381 (M^+ − TsNH), 238, 158 and 104 (100) (Found: C, 67.1; H, 3.85; N, 2.5; S, 5.9. $C_{31}H_{21}NO_7S$ requires C, 67.5; H, 3.85; N, 2.55; S, 5.8%). Evaporation of the organic filtrate and column chromatography of the residue gave (*i*) unchanged tosyl azide **1** (0.7 mmol, 35% recovery) and (*ii*) phenol (0.8 mmol, 80%). A strictly comparable yield of the isolated compound **7** (and phenol) was similarly obtained when the dione **2c** (1 mmol) was treated at room temperature with the azide **1** (3 mmol) in diethyl ether (20 cm^3) in the presence of Et_3N (1 mmol) (20 h).

Reaction of tosyl azide 1 with 2-phenylsulfanyl-2,3-dihydro-1*H*-indane-1,3-dione 2d

(a) In THF in the presence of Et_3N. To a solution of the azide **1** (2.55 mmol) and the dione **2d** (0.85 mmol) in THF (3 cm^3) was slowly added, at room temperature, Et_3N (0.85 mmol) dissolved in THF (2 cm^3). The resulting mixture was stirred at 50 °C (in a sealed tube) for *ca.* 20 h, whereupon it was concentrated under reduced pressure. Column chromatography of the residue separated (*i*) diphenyl disulfide (0.33 mmol, 77%); (*ii*) phenyl toluene-4-thiosulfonate (0.19 mmol, 22%); (*iii*) 2-diazo-2,3-dihydro-1*H*-indane-1,3-dione **12** (0.31 mmol, 36%) and (iv) toluene-*p*-sulfonamide (0.33 mmol, 40%).

In a control experiment a mixture of *N*-tosylbenzenesulfenamide (1 mmol) and Et_3N (1 mmol) in THF (5 cm^3) was stirred at 50 °C (in a sealed tube) for *ca.* 10 h, after which the excess of solvent was evaporated. The solid residue was treated with 10% hydrochloric acid and then extracted several times with diethyl ether. Evaporation of the combined ethereal extracts and subsequent column chromatography gave (*i*) diphenyl disulfide (0.22 mmol, 73%); (*ii*) phenyl toluene-4-thiosulfonate (0.15 mmol, 25%); (*iii*) unchanged *N*-tosylbenzenesulfenamide (0.40 mmol, 40% recovery) and (*iv*) toluene-*p*-sulfonamide (0.45 mmol, 75%).

(b) In HMPA. A mixture of the tosyl azide **1** (1 mmol) and the indanedione **2d** (1 mmol) in HMPA (0.5 cm^3) was stirred at room temperature for 6 h, whereupon it was treated with diethyl ether (10 cm^3) to give a pale-yellow precipitate. This was collected and shown to be 4-*hydroxy*-3-*phenylsulfanyl*-1-*tosylimino*-1H-2-*benzopyran* **15** (0.7 mmol, 70%), mp 196–198 °C (MeOH); ν_{max}/cm^{-1} 3445, (OH) and 1568 (C=N); δ_H 2.28 (3 H, s), 5.86 (1 H, s, removed upon D_2O shaking), 7.02 (2 H, d, *J* 8.2), 7.18–7.31 (5 H, br s), 7.52–7.85 (3 H, m), 7.88 (2 H, d, *J* 8.2) and 8.40 (1 H, d); δ_C 20.45 (q), 121.9 (s), 130.3 (s), 132.5 (s), 134.0 (s), 138.3 (s), 143.2 (s), 144.8 (s), 159.3 (s) and aromatic CH carbons; *m/z* 423.0592 (M^+. $C_{22}H_{17}NO_4S_2$ requires *M*, 423.0599), 314, 155, 130, 109, 91 (100%) and 65 (Found: C, 62.3; H, 4.1; N, 3.35; S, 15.25. $C_{22}H_{17}NO_4S_2$ requires C, 62.4; H, 4.05; N, 3.3; S, 15.15%).

A solution of compound **15** (0.17 mmol) in absolute methanol (20 cm^3) was treated with excess of ethereal diazomethane, at room temperature, to give 4-*methoxy*-3-*phenylsulfanyl*-1-*tosylimino*-1H-2-*benzopyran* **16** (0.6 mmol, 100%), mp 152–154 °C (MeOH); ν_{max}/cm^{-1} 2830 and 1570 (C=N); δ_H 2.32 (3 H, s), 3.89 (3 H, s), 7.11 (2 H, d, *J* 8.6), 7.25–7.37 (3 H, m), 7.37–7.42 (2 H, m), 7.47–7.80 (3 H, m), 7.87 (2 H, d, *J* 8.6) and 8.35 (1 H, d, *J* 8.1); *m/z* 437.0746 (M^+. $C_{23}H_{19}NO_4S_2$ requires *M*, 437.0755), 282, 267, 218, 155 and 130 (100%).

A solution of compound **15** (0.307 mmol) in acetic anhydride (8 cm^3) was refluxed for 1 h, after which water (10 cm^3) was added and the mixture was further refluxed for 10 min. The resulting mixture was then poured into water (50 cm^3) and extracted several times with diethyl ether. Evaporation of the combined ethereal extracts gave the 4-*acetoxy*-3-*phenylsulfanyl*-1-*tosylimino*-1H-2-*benzopyran* **17** (0.256 mmol, 83%), mp 140–141 °C (EtOH); ν_{max}/cm^{-1} 1785 (C=O) and 1580 (C=N); δ_H 2.39 (3 H, s), 2.44 (3 H, s), 7.22 (2 H, d, *J* 8.8), 7.36–7.84 (8 H, m), 7.89 (2 H, d, *J* 8.8) and 8.36 (1 H, d, *J* 8.0); δ_C 20.3 (q), 21.4 (q), 122.15 (s), 130.4 (s), 132.2 (s), 136.5 (s), 138.6 (s), 143.7 (s), 144.1 (s), 158.2 (s), 168.4 (s) and aromatic CH carbons; *m/z* 465.0719 (M^+. $C_{24}H_{19}NO_5S_2$ requires *M*, 465.0705), 423, 240, 130 (100%), 110 and 109.

X-Ray crystal structure analysis of the dimeric indanedione 7

Crystal data. $C_{31}H_{21}NO_7S$, $M = 551.1$, colourless prismatic crystals, triclinic, space group $P\bar{1}$, $a = 11.443(2)$, $b = 13.431(2)$, $c = 10.091(1)$ Å, $\alpha = 98.87(5)$, $\beta = 110.03(5)$, $\gamma = 66.88(5)°$, $V = 1339.7(3)$ Å^3 (by least squares fitting of the goniometric angles of 24 automatically centred reflections), $\lambda = 1.541\,78$ Å, $Z = 2$, $D_x = 1.367$ g cm^{-1}, μ(Cu-Kα) = 1.504 mm^{-1}, $F(000) = 572$.

Data collection and processing. Siemens AED automatized diffractometer, θ–2θ scan, scan width 1.2 + 0.34 tan θ, scan speed 0.05–0.16° s^{-1}, Ni-filtered Cu-Kα radiation, 5073 unique measured reflections, $3 < \theta < 35°$, ($\pm h$, $\pm k$, l), corrected for Lorentz and polarization effects, utilized in the structure analysis.

Structure analysis and refinement. The structure was solved by direct methods with SIR92[11] and refined by full-matrix least-squares on F^2 with SHELXL-93[12] with anisotropic thermal parameters for the non-hydrogen atoms. H atoms were located from a ΔF map and, with the exception of H(1N) which is involved in hydrogen bonding, refined with constrained geometry and isotropic *U*s fixed at $1.2U_{iso}$ of the corresponding C atoms. Final agreement factors were $R_1 = 0.043$, and $wR_2 = 0.123$ for 3192 reflections with $I > 2\sigma(I)$, $R_1 = 0.081$ and $wR_2 = 0.152$ for all data $\{w = 1/\sigma^2(F^2) + 0.1431P^2$, $P = 1/3$ [max. $(F_o^2, 0) + 2F_c^2]$, $\sigma^2(F^2)$ from counting statistics$\}$, $S = 0.706$ for 362 parameters and 5073 reflections. Maximum $\Delta/\sigma = 0.024$, maximum and minimum residual peaks in the final difference Fourier map 0.493 and −0.421 e Å^{-3}. The molecular structure of **7** is shown in Fig. 1. The two indanedione moieties, which are interconnected by a single C–C bond, tend to face, forming an angle of ≈23° between the planes defined by the two corresponding six-membered rings. However the two indanedione moieties are tilted ≈55° along the C(1)–C(10) bond for minimizing repulsive interactions. The five-membered rings have an envelope conformation, with the apical carbon [C(1) and C(10), respectively] and the oxygen atoms lying on opposite sites with respect to the plane defined by the remaining four C atoms. The C(2)–C(1)–C(9) and C(11)–C(10)–C(18) bond angles are significantly reduced from the tetrahedral value to 101.7(2) and 102.5(2)°, respectively. The crystal structure is characterized by the formation, *via* a double intermolecular centrosymmetric hydrogen bond H(1N)•••O(1′), of dimeric units (Fig. 1), whose packing is mainly determined by van der Waals interactions. Listings of atomic coordinates,

bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.†

X-Ray crystal structure analysis of the acetoxybenzopyran 17

Crystal data. $C_{24}H_{19}NO_5S_2$, $M = 465.1$, colourless prismatic crystals, orthorhombic, space group $P2_12_12_1$, $a = 15.089(3)$, $b = 15.688(3)$, $c = 9.378(2)$ Å, $V = 2219.9(8)$ Å^3 (by least-squares fitting of the goniometric angles of 24 automatically centred reflections), $\lambda = 1.541\,78$ Å, $Z = 4$, $D_x = 1.393$ g cm^{-1}, μ(Cu-Kα) = 2.487 mm^{-1}, $F(000) = 968$.

Data collection and processing. Siemens AED automatized diffractometer, θ–2θ scan, scan width $1.2 + 0.34 \tan\theta$, scan speed 0.05–0.16° s^{-1}, Ni-filtered Cu-Kα radiation, 2404 unique measured reflections, $3 < \theta < 35°$, ($\pm h$, $\pm k$, l), corrected for Lorentz and polarization effects, utilized in the structure analysis.

Structure analysis and refinement. The structure was solved by direct methods with SIR92[11] and refined by full-matrix least-squares on F^2 with SHELXL-93[12] with anisotropic thermal parameters for the non-hydrogen atoms. H atoms were located from a ΔF map and refined with constrained geometry and isotropic Us fixed at $1.2U_{iso}$ of the corresponding C atoms. Final agreement factors were $R_1 = 0.035$, and $wR_2 = 0.073$ for 1272 reflections with $I > 2\sigma(I)$, $R_1 = 0.085$ and $wR_2 = 0.913$ for all data {$w = 1/\sigma^2(F^2) + 0.389P^2$, $P = 1/3$ [max. (F_0^2, 0) + $2F_c^2$], $\sigma^2(F^2)$ from counting statistics}, $S = 0.838$ for 290 parameters and 2404 reflections. Maximum $\Delta/\sigma = 0.031$, maximum and minimum residual peaks in the final difference Fourier map 0.157 and −0.173 e Å^{-3}. The molecular structure of **17** is shown in Fig. 2. The crystal packing is mainly determined by van der Waals interactions. Listings of atomic coordinates, bond lengths and bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.†

† For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1995, Issue 1.

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