The Thermal Elimination of Iodine from Some Substituted α-Iodonaphthalenes: a Structural Study

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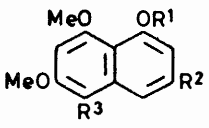
Brief heating of a number of methyl 8-iodo-5,7-dimethoxy-2-naphthoate derivatives with a variety of added hydroxy-, methoxy-, or acetoxy-substituents in the 4- and 6-positions has been found to result in facile elimination of iodine in certain compounds but not others; subsequent examination of other aspects of the chemistry of the system have suggested this to be a solid state effect. Single crystal *X*-ray structure determinations have been carried out on a representative selection of compounds, suggesting that in those examples where elimination has been found to occur, intimate charge-transfer interactions between the conjugated systems of adjacent molecules arising from the nature of the crystal packing are responsible; in those compounds which do not eliminate iodine, similar interactions may also be found but are associated with substituent out-of-plane steric interactions which hinder relative movement of the naphthalene moieties in the lattice.

BRIEF heating of a crystalline sample of the iodonaphthalene (1) at 120°, well below its m.p., resulted in efficient conversion into the dimer (2) [1,2] and the liberation of iodine. In preparative work yields of up to 80% have been obtained. The mildness of these conditions compared with the severity of analogous Ullmann reactions,[3-5] suggested the involvement of a solid state effect.[6,7] So too did the fact that the process could not be brought about in solution in neutral organic media.

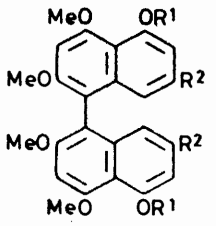
At the molecular level the reaction evidently requires a catalytic source of protons or of an equivalent electrophile. Fresh alkali-washed samples of compound (1) were stable to heating initially but on storage they progressively regained the capacity for efficient dimerization.

Dissolving compound (1) in trifluoroacetic acid at room temperature also caused rapid liberation of iodine. However under these conditions the yield of dimer (2) was comparatively low (32%) and there was significant conversion into the deiodinated monomer (3) [2] (21%).

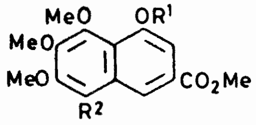
These observations are consistent with the reaction sequence in the Scheme, where the process is initiated by electrophilic attack. Formation of the dimer (2) would



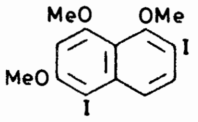
(1) R^1 = Me, R^2 = CO_2Me, R^3 = I
(3) R^1 = Me, R^2 = CO_2Me, R^3 = H
(4) R^1 = Ac, R^2 = CO_2Bu^t, R^3 = I
(5) R^1 = H, R^2 = CO_2Bu^t, R^3 = I
(6) R^1 = Ac, R^2 = CO_2Me, R^3 = I
(7) R^1 = H, R^2 = CO_2Me, R^3 = I
(8) R^1 = Me, R^2 = CO_2H, R^3 = I
(9) R^1 = Me, R^2 = H, R^3 = I
(15) R^1 = H, R^2 = CO_2Me, R^3 = H
(17) R^1 = Ac, R^2 = CO_2Bu^t, R^3 = H
(18) R^1 = H, R^2 = CO_2Bu^t, R^3 = H
(19) R^1 = Ac, R^2 = CO_2Me, R^3 = H



(2) R^1 = Me, R^2 = CO_2Me
(13) R^1 = Me, R^2 = CO_2H
(14) R^1 = Me, R^2 = H
(16) R^1 = H, R^2 = CO_2Me



(11) R^1 = Ac, R^2 = I
(12) R^1 = Me, R^2 = I
(20) R^1 = Me, R^2 = H



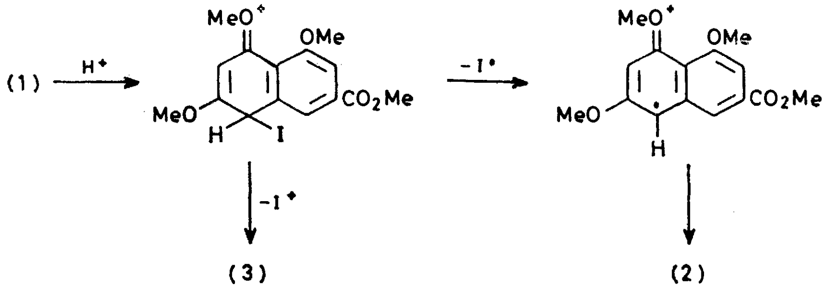
(10)

involve homolysis of the carbon–iodine bond and coupling of the resulting cation radical. However, the effectiveness with which this competes with deiodination to (3) depends on the reaction conditions and most particularly on the nature of the crystal packing. The significance of this latter factor has been strikingly borne out by the differing behaviour of nine closely related α-iodonaphthalene derivatives (4)—(12).

Compounds (4)—(10) were synthesised by simple adaptation of a Stobbe reaction between 3,5-dimethoxybenzaldehyde and dimethyl succinate [2] while compounds (11) and (12) were similarly prepared from 3,4,5-trimethoxybenzaldehyde.[8] Introduction of the iodo-substituent(s) was by direct substitution at a late stage of each synthesis. Details are given in the Experimental section.

The new iodo-compounds all melted in essentially the same region as compound (1). However, six of them either decomposed without elimination of iodine on melting [(4), (5)] or were quite stable at their m.p.s [(6), (10), (11), (12)]; four of these [(4), (5), (6), (11)] could be forced to lose iodine by being heated to temperatures well above their m.p.s but these processes were quite inefficient and non-specific. Crystals of the three remaining iodo-derivatives (7)—(9) readily lost iodine on being heated briefly under conditions similar to those employed for compound (1). Compounds (8) and (9) were thereby converted into their respective dimers (13) and (14) in yields of 50 and 48%. The hydroxy-compound (7) underwent more extensive decomposition, affording a comparatively poor yield of isolable product. This consisted chiefly of the deiodinated monomer (15) (20%) with only limited recovery of the dimer (16) (5%). Under the same conditions compound (1) gave mostly the dimer (2) (68%) and very little of the deiodinated monomer (3) (5%). All three compounds (7)—(9), like (1), were stable to being heated in neutral organic solution.

The widely differing behaviour of the iodo-compounds described in this work cannot be correlated with obvious electronic effects since all, with the exception of compounds (11) and (12), are structurally uniform in the reactive iodine-containing ring. A representative selection, consisting of compounds (1) [1] and (7) (both thermally reactive) and of compounds (6) and (10)—(12) (all thermally unreactive) have therefore been subjected to single crystal *X*-ray structure determination in order to assess the basis of effects in the solid state.



SCHEME

EXPERIMENTAL

Unless otherwise stated i.r. spectra were measured as KBr discs, electronic spectra in chloroform, and ^1H n.m.r. spectra in $CDCl_3$. Chemical shifts are quoted on the δ scale from $SiMe_4$ as internal reference. T.l.c. was carried out on Merck silica gel GF_{254} in toluene–ethyl acetate (3 : 1).

t-Butyl 4-Acetoxy-5,7-dimethoxy-2-naphthoate (17).—Stobbe reaction between 3,5-dimethoxybenzaldehyde and dimethyl succinate [2] was carried out in the presence of potassium t-butoxide. A minor component eluted from silica with toluene–ethyl acetate (12 : 1) was crystallized from ethanol to give fine, pale yellow needles of *t-butyl 4-acetoxy-5,7-dimethoxy-2-naphthoate* (17) (2%), m.p. 127—129° (Found: C, 66.1; H, 6.7. $C_{19}H_{22}O_6$ requires C, 65.9; H, 6.4%), $\lambda_{max.}$ 281, 285sh, 300sh, 338sh, 349, 363, and 393 nm (log ε 3.88, 3.86, 3.52, 3.39, 3.42, 3.43, and 2.55), $\nu_{max.}$ 1 755, 1 745, 1 710, 1 630, 1 615, 1 586, and 1 508 cm^{-1}, δ 1.62 [s, $OC(CH_3)_3$], 2.37 (s, $OCOCH_3$), 3.91br (s, 2 × OCH_3), 6.58 (d, *J* 2 Hz, H-6), 6.85 (d, *J* 2 Hz, H-8), 7.43 (d, *J* 1.5 Hz, H-3), and 8.24 (d, *J* 1.5 Hz, H-1), *m/e* 346 (M^+, 10), 304 (9), and 248 (100%).

t-Butyl 4-Acetoxy-8-iodo-5,7-dimethoxy-2-naphthoate (4).—The foregoing ester (17) (100 mg) was iodinated with iodine and mercury(II) acetate in acetic acid [2,8] to give a yellow oil. This was purified by preparative t.l.c. to give *t-butyl 4-acetoxy-8-iodo-5,7-dimethoxy-2-naphthoate* (4) (112 mg, 82%), pale yellow platelets, m.p. 119° (decomp. without elimination of iodine) (from ethanol) (Found: C, 48.3; H, 4.4. $C_{19}H_{21}IO_6$ requires C, 48.3; H, 4.5%), $\lambda_{max.}$ 292, 305, 318, 367, and 374sh nm (log ε 3.64, 3.71, 3.74, 3.65, and 3.62), $\nu_{max.}$ 1 765, 1 707, 1 619, 1 599, 1 560, and 1 506 cm^{-1}, δ 1.64 [s, $OC(CH_3)_3$], 2.38 (s, $OCOCH_3$), 3.98 and 4.01 (s, s, 2 × OCH_3), 6.71 (s, H-6), 7.50 (d, *J* 1.5 Hz, H-3), and 8.84 (d, *J* 1.5 Hz, H-1), *m/e* 472 (M^+, 40), 430 (19), 416 (9), and 374 (100%).

t-Butyl 4-Hydroxy-5,7-dimethoxy-2-naphthoate (18).—A solution of potassium hydroxide (2.5 g) in water (10 cm^3) heated at 50 °C was carefully added to a similarly heated solution of the diester (17) (0.10 g) in methanol (15 cm^3) under nitrogen. This solution was stirred under nitrogen at 50° for 40 min. Isolation of the product gave a fawn oil which crystallized on standing. Recrystallization from ethanol afforded pale fawn rectangular prisms of *t-butyl 4-hydroxy-5,7-dimethoxy-2-naphthoate* (18) (84 mg, 96%), m.p. 117.5—119.5° (Found: C, 66.8; H, 6.7. $C_{17}H_{20}O_5$ requires C, 67.1; H, 6.6%), $\lambda_{max.}$ 283, 291, 305, 344sh, 356, and 372 nm (log ε 3.81, 3.75, 3.60, 3.45, 3.64, and 3.65),

$\nu_{max.}$ 3 437, 1 713, 1 621, 1 584, and 1 512 cm^{-1}, δ 1.62 [s, OC(CH$_3$)$_3$], 3.90 and 4.04 (s, s, 2 × OCH$_3$), 6.53 (d, *J* 2 Hz, H-6), 6.80 (d, *J* 2 Hz, H-8), 7.25 (d, *J* 1.5 Hz, H-3), 7.86 (d, *J* 1.5 Hz, H-1), and 9.12 (s, OH, exchanged with D$_2$O), *m/e* 304 (M^+, 22) and 248 (100%).

t-Butyl 4-*Hydroxy*-8-*iodo*-5,7-*dimethoxy*-2-*naphthoate* (5).—The foregoing ester (18) (50 mg) was iodinated, as for (17), to give *t-butyl* 4-*hydroxy*-8-*iodo*-5,7-*dimethoxy*-2-*naphthoate* (5) (57 mg, 81%). It could not be recrystallized or sublimed without decomposition. Purification by preparative t.l.c. afforded small, pale yellow crystals, m.p. 146.5—148.5° (decomp. without elimination of iodine) (Found: *m/e*, 430.027 9. $C_{17}H_{19}IO_5$ requires *M*, 430.027 9), $\lambda_{max.}$ 294, 308, 321, 371, and 381sh nm (log ε 3.62, 3.73, 3.76, 3.75, and 3.70), $\nu_{max.}$ 3 417, 1 707, 1 626, 1 606, 1 566, and 1 510 cm^{-1}, δ 1.64 [s, OC(CH$_3$)$_3$], 4.00 and 4.09 (s, s, 2 × OCH$_3$), 6.62 (s, H-6), 7.32 (d, *J* 1.5 Hz, H-3), 8.39 (d, *J* 1.5 Hz, H-1), and 9.25 (s, OH, exchanged with D$_2$O), *m/e* 430 (M^+, 34) and 374 (100%).

Methyl 4-*Acetoxy*-8-*iodo*-5,7-*dimethoxy*-2-*naphthoate* (6).—This was obtained, in 90% yield, by iodination of the diester (19),[2] as for (17). Recrystallization from ethanol gave colourless prisms of the *iodo-acetate* (6), m.p. 162.5—163.5° (Found: C, 44.7; H, 3.6. $C_{16}H_{15}IO_6$ requires C, 44.7, H, 3.5%), $\lambda_{max.}$ 293, 304, 318, 370, and 379sh nm (log ε 3.64, 3.73, 3.74, 3.66, and 3.64), $\nu_{max.}$ 1 760, 1 720, 1 618, 1 600, 1 559, and 1 507 cm^{-1}, δ 2.33 (s, OCOCH$_3$), 3.95 (s, 2 × OCH$_3$), 3.98 (s, OCH$_3$), 6.69 (s, H-6), 7.53 (d, *J* 2 Hz, H-3), and 8.84 (d, *J* 2 Hz, H-1), *m/e* 430 (M^+, 43) and 388 (100%).

Needles for *X*-ray study were grown by slow evaporation of methanol solutions at room temperature.

Methyl 4-*Hydroxy*-8-*iodo*-5,7-*dimethoxy*-2-*naphthoate* (7).—The iodo-acetate (6) (46 mg) was boiled for 15 min. under nitrogen in a solution of sodium (32 mg) in freshly distilled methanol (5 cm^3). Isolation of the product gave *methyl* 4-*hydroxy*-8-*iodo*-5,7-*dimethoxy*-2-*naphthoate* (7) (38 mg, 92%) as fine, fawn needles from ethanol which decomposed without melting at 101°, m.p. after washing with aqueous NaOH *ca.* 150° (Found: C, 43.4; H, 3.6. $C_{14}H_{13}IO_5$ requires C, 43.3; H, 3.4%), $\lambda_{max.}$ 294, 308, 322, 374, and 387 nm (log ε 3.70, 3.76, 3.76, 3.77, and 3.76), $\nu_{max.}$ 3 375, 1 716, 1 623, 1 607, 1 568, and 1 508 cm^{-1}, δ 3.97, 4.02, and 4.13 (s, s, s, 3 × OCH$_3$), 6.68 (s, H-6), 7.38 (d, *J* 2 Hz, H-3), 8.42 (d, *J* 2 Hz, H-1), and 9.31 (s, OH, exchanged with D$_2$O), *m/e* 388 (M^+, 100%).

Fawn needles, for *X*-ray study, were grown by slow evaporation of acetone solutions at room temperature.

8-*Iodo*-4,5,7-*trimethoxy*-2-*naphthoic Acid* (8).—Alkaline hydrolysis of the ester (1) [2] afforded a crystalline material (88 mg, 91%). Recrystallization from ethanol gave golden needles of 8-*iodo*-4,5,7-*trimethoxy*-2-*naphthoic acid* (8) which decomposed at 115° without melting (Found: C, 43.4; H, 3.6. $C_{14}H_{13}IO_5$ requires C, 43.3; H, 3.4%), $\lambda_{max.}$ 294, 305, 319, and 377 nm (log ε 3.76, 3.77, 3.76, and 3.77), $\nu_{max.}$ 2 850, 1 674, 1 592, 1 570, and 1 508 cm^{-1}, δ(C$_5$D$_5$N) 3.89, 3.93, and 3.94 (s, s, s, 3 × OCH$_3$), 6.86 (s, H-6), 8.01 (d, *J* 1.5 Hz, H-3), and 9.41 (d, *J* 1.5 Hz, H-1), *m/e* 388 (M^+, 100%).

Iodination of 1,3,8-*Trimethoxynaphthalene*.—1,3,8-Trimethoxynaphthalene [2,9] (68 mg) was treated with a molar equivalent of iodine, as for (17). Two products were separated chromatographically in toluene–ethyl acetate (4 : 1). Recovery of the more mobile band gave needles of 1,6-*di-iodo*-2,4,5-*trimethoxynaphthalene* (10) (17 mg, 12%), m.p. 122.5—124° (from ethanol) (Found: C, 33.2; H, 2.7. $C_{13}H_{12}I_2O_3$ requires C, 33.2; H, 2.6%), $\lambda_{max.}$ 306, 319, 348, 356sh, and 408 nm (log ε 3.91, 3.93, 3.71, 3.67, and 3.02), $\nu_{max.}$ 1 600, 1 572, and 1 548 cm^{-1}, δ 3.83 (s, 5-OCH$_3$), 4.02 and 4.04 (s, s, 2 × OCH$_3$), 6.67 (s, H-3), and 7.76 and 7.79 (ABq, *J* 9 Hz, H-7, -8), *m/e* 470 (M^+, 100%).

The less mobile band gave 1-*iodo*-2,4,5-*trimethoxynaphthalene* (9) (63 mg, 59%) as a crystalline solid which decomposed without melting at 72° and coloured on standing, m.p. after washing with aqueous NaOH *ca.* 115°. It could not be recrystallized or sublimed without decomposition. Spectral data were obtained immediately following isolation (Found: *m/e*, 343.991 1. $C_{13}H_{13}IO_3$ requires *M*, 343.991 1), $\lambda_{max.}$ 303, 315, 339, and 348 nm (log ε 3.87, 3.92, 3.81, and 3.79), $\nu_{max.}$ 1 611, 1 589, and 1 573 cm^{-1}, δ 3.95, 3.99, and 4.00 (s, s, s, 3 × OCH$_3$), 6.64 (s, H-3), 6.77br (d, *J* 8 Hz, H-6), 7.40 (t, *J* 8 Hz, H-7), and 7.81 (dd, *J* 8, 1 Hz, H-8), *m/e* 344 (M^+, 100%).

Methyl 4-*Acetoxy*-8-*iodo*-5,6,7-*trimethoxy*-2-*naphthoate* (11).—This compound was prepared in 68% yield by the method of Bell and Weiss.[8] Irregular cream plates were obtained on recrystallization from aqueous methanol, m.p. 92—94° (lit.,[8] 112—113°) (Found: C, 44.4; H, 3.8. Calc. for $C_{17}H_{17}IO_7$: C, 44.4; H, 3.7%), $\lambda_{max.}$ 314, 342, and 354 nm (log ε 3.80, 3.54, and 3.60), $\nu_{max.}$ 1 768, 1 725, and 1 585 cm^{-1}, δ 2.39 (s, OCOCH$_3$), 3.93, 3.97, 3.99, and 4.00 (s, s, s, s, 4 × OCH$_3$), 7.66 (d, *J* 1.5 Hz, H-3), and 8.84 (d, *J* 1.5 Hz, H-1), *m/e* 460 (M^+, 70) and 418 (100%).

Slow evaporation of ethanol solutions gave prismatic crystals for *X*-ray study.

Methyl 8-*Iodo*-4,5,6,7-*tetramethoxy*-2-*naphthoate* (12).—The ester (20) was prepared according to the literature,[8] m.p. 104—104.5° (lit.,[8] 104—104.5°). Iodination as for (17) gave *methyl* 8-*iodo*-4,5,6,7-*tetramethoxy*-2-*naphthoate* (12) (66%), m.p. 93—94.5°, fine needles from aqueous ethanol (Found: C, 44.3; H, 4.0. $C_{16}H_{17}IO_6$ requires C, 44.5; H, 4.0%), $\lambda_{max.}$ 311, 321, 348, and 362 nm (log ε 3.78, 3.76, 3.64, and 3.67). $\nu_{max.}$ 1 715, 1 610, 1 580, and 1 567 cm^{-1}, δ 3.92, 3.99, 4.00, 4.01, and 4.06 (s, s, s, s, s, 5 × OCH$_3$), 7.41 (d, *J* 1.5 Hz, H-3), and 8.56 (d, *J* 1.5 Hz, H-1), *m/e* 432 (M^+, 100%).

Slow evaporation of aqueous ethanol solutions, gave fine needles for *X*-ray study.

Methyl 4-*Hydroxy*-5,7-*dimethoxy*-2-*naphthoate* (15).—The ester (19) [2] (31 mg) was treated with sodium methoxide as for (6). Recrystallization of the product from ethanol gave clusters of needles of *methyl* 4-*hydroxy*-5,7-*dimethoxy*-2-*naphthoate* (15) (25 mg, 94%), m.p. 160—161° (Found: C, 64.0; H, 5.5. $C_{14}H_{14}O_5$ requires C, 64.1; H, 5.4%), $\lambda_{max.}$ 284, 292, 306, 344sh, 357, and 374 nm (log ε 3.82, 3.78, 3.55, 3.40, 3.63, 3.65), $\nu_{max.}$ 3 375, 1 715, 1 618, 1 587, and 1 506 cm^{-1}, δ 3.90, 3.94, and 4.04 (s, s, s, 3 × OCH$_3$), 6.55 (d, *J* 2 Hz, H-6), 6.81 (d, *J* 2 Hz, H-8), 7.29 (d, *J* 1.5 Hz, H-3), 7.93 (d, *J* 1.5 Hz, H-1), and 9.15 (s, OH, exchanged with D$_2$O), *m/e* 262 (M^+, 100%).

Elimination of Iodine from Compound (7).—Crystalline compound (7) (30 mg) was heated at 120° for 6 min. Iodine sublimed from the crystals within the first 30 s. The residue was dissolved in chloroform, washed with 10% aqueous sodium thiosulphate, and the organic phase separated by t.l.c. to give three major constituents. Two bands with R_F 0.49 and 0.40 were identified as deiodinated compound (15) (4 mg, 20%), mixed m.p. 160—161°, and as starting material (7) (1.7 mg, 6%), respectively, both indistinguishable from authentic materials in i.r. absorption and chromatographic behaviour.

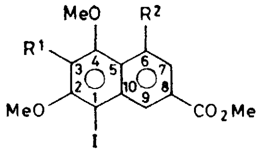
The third band, R_F 0.23, gave rise to *dimethyl* 5,5′-*dihydroxy*-2,2′,4,4′-*tetramethoxy*-1,1′-*binaphthalene*-7,7′-*dicarboxylate* (16) (1 mg, 5%), m.p. 296—297.5° (decomp.) (Found: *m/e*, 522.152 4. $C_{28}H_{26}O_{10}$ requires *M*, 522.152 6), $\lambda_{max.}$ 291, 305, 317, 378, and 391 nm (log ε 3.81, 3.76, 3.73, 3.80, and 3.81), $\nu_{max.}$ 3 420, 1 722, 1 604, 1 574, 1 558, and 1 510 cm^{-1}, δ 3.74 (s, 2 × OCH_3), 3.76 (s, 2 × OCH_3), 4.19 (s, 2 × *peri*-OCH_3), 6.86 (s, H-3, -3′), 7.29 (m, H-6, -6′, -8, -8′) and 9.38 (s, 2 × OH, exchanged with D_2O), *m/e* 522 (M^+, 100%).

Elimination of Iodine from Compound (8).—Crystalline compound (8) (27 mg) was heated at 150° for 7 min and treated as for the reaction of (7) except that the crude product was worked up and chromatographed in ethyl acetate. This gave the dimer diacid (13) (9 mg, 50%) as pale yellow needles, m.p. 322° (decomp.) (lit.,[2] 322—326°). Also isolated was unchanged iodo-acid (8) (3 mg, 11%), decomp. 115°. Both products were indistinguishable from authentic materials in chromatographic behaviour and in i.r. and u.v. absorption.

Elimination of Iodine from Compound (9).—Crystalline compound (9) (20 mg) was heated at 105° for 2 min. Iodine was rapidly eliminated. The residue was worked up as for the reaction of (7) to give the dimer (14) (6 mg, 48%), as microneedles, m.p. 270—272°, having the same R_F, i.r. absorption, and ^1H n.m.r. spectrum as authentic material.[2] A very minor band was formulated as 1,3,8-trimethoxynaphthalene (0.3 mg) by comparison of fluorescence under u.v. light and R_F with authentic material.[2,9]

Iodine was also released from crystalline compound (9) on standing at room temperature for >48 h. The dimer (14) was identified, by t.l.c., as the major product.

Crystallography.—Specific details peculiar to each compound are given in Table 1. General details are as follows. In each case a unique data set was measured within a preset $2\theta_{max.}$ limit using either a Syntex $P\bar{1}$ or $P2_1$ four-circle diffractometer in conventional 2θ—θ scan mode yielding $n(I)$ independent reflections; of these $n(I_0)$ with $I > 3\sigma(I)$ were considered ' observed ' and used in the refinement of the structure after solution by the heavy atom method. Monochromatic Mo-K_α radiation was used and data were corrected for absorption. Refinement in each case was basically 9 × 9 block diagonal least squares procedures, the thermal motion of the non-hydrogen atoms being refined anisotropically. Where the quality of the data permitted, hydrogen atom positional parameters were refined in the same block as the parent carbon, otherwise they were located in difference maps and ' improved ' by estimation to constrained trigonal or tetrahedral sites. U_H (isotropic) were constrained in the refinement at 1.5 < U_{ii} (parent C,O) > ($-CH_3$, $-OH$), or 1.25 <U_{ii} (parent C)>. Reflection weights throughout were set at $[\sigma^2(F_0) + 0.000\,3(F_0)^2]^{-1}$. Neutral atom scattering factors were used, those for I, C, and O being corrected for anomalous dispersion (f', f'').[10-12] Computation was carried out using the *X*-RAY 76 program system.[13] Material deposited comprises tables of structure factor amplitudes, thermal parameters, and hydrogen atom geometries.* Atom numbering adopted follows that used in the earlier study [1] for compound (1) (Figure 1). The material used in this study was of poor quality for crystallographic work, being fragile very thin plates.



(1) R^1 = H, R^2 = OMe
(7) R^1 = H, R^2 = OH } Eliminate I_2 on heating
(6) R^1 = H, R^2 = OAc
(12) R^1 = OMe,R^2 = OMe } Stable on heating to m.p.
(11) R^1 = OMe,R^2 = OAc
(10) R^1 = H, R^2 = OMe; I, H at positions 7,8; also 'stable

FIGURE 1 The numbering of the ring system adopted for the crystallographic work following that previously used for (1) [1] is shown. The carbon and oxygen atoms appended at ring atom C(*n*) are labelled C,O(*nm*) (*m* = 1,2) depending on their position in the substituent string. Hydrogen atoms are numbered according to the parent carbon; where more than one is present they are distinguished by suffixes A—C. In the cell diagrams, carbon atoms are identified by number only; the iodines are also identified

DISCUSSION

The crystal structures of five compounds (6), (7), and (10)—(12) and (1), reported elsewhere,[1] have been determined in an attempt to ascertain the origin of the susceptiblity of compounds (1) and (7) to decomposition on heating, relative to the others which are more or less inert, at least to their m.p.s. In examining the structures to this end, the following seem to be the possible features which might reasonably be expected to be important in influencing thermal stability.

(a) *Substituent Effects* (*Electronic*).—Generally this seems an unlikely cause because of the similarity of substitution patterns throughout the series. Nevertheless, if this *were* the case, it might be reasonably expected to be manifest as an abnormally long C(1)–I distance (the value for a ' normal ' aromatic C–I distance does not appear to be clearly established yet, but may be surmised to be *ca.* 2.05—2.10 Å[1]) and/or variations in the ring geometries and the bonding parameters of the associated substituents. The presence of the iodine atoms, and/or variability in the suitability of the available specimens renders detection of meaningful variations in C–I difficult and C–C, O almost impossible throughout the entire series, the precision of the light atom geometries of (6), (10), and (12) being particularly poor. Skeletal geometries are given in Table 6.

(b) *Charge-transfer Interactions*.—These, if present, may be of two types manifested (i) as close I · · · I contacts. The Pauling–van der Waals estimate for a pair of iodine atoms is 4.3 Å;[14] Bondi's estimate[15] of [2 × (1.95—2.05)] Å is rather less. Values are tabulated up to a limit of 4.5 Å; in many cases, the presence of a significant interaction may be doubtful or absent, but the close proximity of a pair of iodine atoms may carry the implication that the molecules are suitably positioned for interaction when the lattice has undergone sufficient thermal excitation, assuming no phase change. Type (ii) constituting close interplanar contacts between the naphthalene skeleton planes of adjacent molecules,

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TABLE 1

Individual crystallographic parameters

Formula	(7)	(6)	(12)	(11)	(10)
Formula	$C_{14}H_{13}IO_5$	$C_{16}H_{15}IO_6$	$C_{16}H_{17}IO_6$	$C_{17}H_{17}IO_7$	$C_{13}H_{12}I_2O_3$
M	388.2	430.2	432.2	460.2	470.0
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n(C_{2h}^5$, No. 14)	$P2_1/a$	$P2_1/a$	$P\bar{1}(C_i^1$, No. 2)	$P2_1/n$
a/Å	5.046(4)	7.741(4)	14.890(6)	19.075(6)	20.489(13)
b/Å	17.840(6)	20.586(10)	20.390(6)	11.515(4)	7.591(3)
c/Å	15.689(5)	10.627(6)	11.896(4)	8.540(5)	21.579(12)
α/°				104.46(3)	
β/°	96.16(5)	101.67(5)	111.05(3)	91.19(4)	118.98(3)
γ/°				96.97(4)	
U/Å^3	1 404(1)	1 658(2)	3 371(2)	1 800(2)	2 936(3)
D_m/g cm^{-3}	1.84(1)	1.71(1)		1.69(1)	2.10(1)
D_c/g cm^{-3}	1.84	1.72	1.70	1.70	2.13
Z	4	4	8	4	8
F(000)	760	848	1 712	912	1 760
$2\theta_{max.}$/°	50	40	40	50	37.5
$n(I)$	2 457	1 559	3 169	4 732	2 289
$n(I_0)$	1 813	1 203	2 047	3 351	1 318
R	0.035	0.083	0.044	0.038	0.038
R'	0.039	0.091	0.049	0.047	0.044
S	1.4	2.2	1.7	1.8	1.1
Specimen size (mm)	0.45 × 0.14 × 0.05	0.25 × 0.25 × 0.05	0.31 × 0.17 × 0.08	0.35 × 0.31 × 0.06	0.02 × 0.47 × 0.06
μ/cm^{-1}	21.7	18.5	18.3	17.2	40.3

TABLE 2

Atomic fractional cell co-ordinates for (6) and (7)

		(7)			(6)	
Atom	x	y	z	x	y	z
I(1)	0.198 37(8)	0.069 13(2)	0.066 86(2)	0.308 4(3)	0.041 77(9)	0.097 5(2)
C(1)	0.227 8(9)	0.140 6(2)	0.173 1(3)	0.281(3)	0.051(1)	0.280(2)
C(2)	0.053 3(9)	0.199 4(3)	0.171 7(3)	0.284(3)	−0.001(1)	0.358(2)
O(2)	−0.128 7(7)	0.206 5(2)	0.101 4(2)	0.327(2)	−0.058 7(7)	0.310 (2)
C(21)	−0.316 0(12)	0.266 8(4)	0.098 6(4)	0.340(4)	−0.119(1)	0.384(3)
H(21A)	−0.420(13)	0.269(4)	0.144(4)	0.372(—)	−0.161(—)	0.352(—)
H(21B)	−0.236(13)	0.319(4)	0.096(4)	0.224(—)	−0.124(—)	0.409(—)
H(21C)	−0.459(13)	0.258(3)	0.041(4)	0.433(—)	−0.109(—)	0.464(—)
C(3)	0.065 1(10)	0.249 9(3)	0.240 8(3)	0.253(3)	0.000(1)	0.481(3)
H(3)	−0.052(10)	0.291(3)	0.237(3)	0.288(28)	−0.032(11)	0.545(19)
C(4)	0.250 7(10)	0.240 5(3)	0.310 0(3)	0.197(3)	0.056(1)	0.531(2)
O(4)	0.268 8(7)	0.287 2(2)	0.379 3(2)	0.155(2)	0.060 4(7)	0.650(11)
C(41)	0.107 0(15)	0.352 5(4)	0.377 4(4)	0.179(3)	0.004(1)	0.732(2)
H(41A)	0.153(14)	0.386(4)	0.336(4)	0.148(—)	0.007(—)	0.817(—)
H(41B)	−0.070(14)	0.340(4)	0.367(5)	0.307(—)	−0.009(—)	0.744(—)
H(41C)	0.136(14)	0.374(4)	0.431(4)	0.105(—)	−0.032(—)	0.683(—)
C(5)	0.434 4(9)	0.179 7(2)	0.315 2(3)	0.191(3)	0.115(1)	0.457(2)
C(6)	0.631 8(10)	0.166 9(3)	0.386 3(3)	0.138(3)	0.176(1)	0.506(2)
O(6)	0.653 6(8)	0.211 7(2)	0.456 8(2)	0.080(2)	0.183 2(7)	0.621(1)
H(6)	0.550(12)	0.250(3)	0.450(4)			
C(61)				0.178(3)	0.187(1)	0.736(2)
O(61)				0.349(2)	0.191 4(9)	0.735(2)
C(62)				0.102(4)	0.184(1)	0.040(2)
H(62A)				Not located		
H(62B)						
H(62C)						
C(7)	0.802 9(10)	0.108 2(3)	0.386 9(3)	0.144(4)	0.231(1)	0.437(3)
H(7)	0.937(11)	0.099(3)	0.435(3)	0.130(40)	0.259(12)	0.457(28)
C(8)	0.790 0(10)	0.058 2(3)	0.317 6(3)	0.188(3)	0.231(1)	0.312(2)
C(81)	0.970 4(10)	−0.008 4(3)	0.318 7(3)	0.209(3)	0.293(1)	0.248(2)
O(81)	0.947 7(9)	−0.057 6(2)	0.266 8(3)	0.196(3)	0.343 7(7)	0.295(2)
O(82)	1.157 8(7)	−0.006 8(2)	0.385 4(2)	0.232(2)	0.284 6(7)	0.128(2)
C(82)	1.338 9(14)	−0.070 0(4)	0.391 4(5)	0.251(4)	0.342(1)	0.056(3)
H(82A)	1.239(13)	−0.120(4)	0.405(4)	0.269(—)	0.338(—)	−0.035(—)
H(82B)	1.425(15)	−0.075(4)	0.343(5)	0.357(—)	0.367(—)	0.104(—)
H(82C)	1.462(15)	−0.058(4)	0.440(5)	0.144(—)	0.370(—)	0.052(—)
C(9)	0.603 7(110)	0.067 9(3)	0.248 1(3)	0.232(3)	0.172(1)	0.267(2)
H(9)	0.584(10)	0.028(3)	0.200(3)	0.226(28)	0.172(10)	0.172(19)
C(10)	0.423 0(9)	0.128 5(2)	0.244 0(3)	0.232(3)	0.113(1)	0.337(2)

TABLE 3

Atomic fractional cell co-ordinates for (12)

	Molecule 1			Molecule 2		
Atom	x	y	z	x	y	z
I(1)	0.079 61(7)	0.164 79(4)	0.238 58(9)	0.215 96(7)	0.533 26(4)	0.390 56(8)
C(1)	0.121 7(7)	0.103 1(5)	0.126 0(9)	0.169 2(5)	0.465 5(5)	0.491 2(10)
C(2)	0.142 9(8)	0.132 0(5)	0.038 0(10)	0.172 4(8)	0.399 9(5)	0.462 1(9)
O(2)	0.140 7(5)	0.200 2(3)	0.023 0(7)	0.208 8(5)	0.380 9(4)	0.374 0(6)
C(21)	0.061 2(10)	0.224 7(6)	−0.073 6(14)	0.137 7(9)	0.364 5(6)	0.259 2(10)
H(21A)	0.062(—)	0.205(—)	−0.151(—)	0.098(—)	0.329(—)	0.270(—)
H(21B)	0.002(—)	0.210(—)	−0.068(—)	0.097(—)	0.402(—)	0.229(—)
H(21C)	0.056(—)	0.270(—)	−0.088(—)	0.163(—)	0.352(—)	0.200(—)
C(3)	0.174 6(8)	0.095 2(5)	−0.041 8(10)	0.139 6(8)	0.352 3(4)	0.523 7(9)
O(3)	0.189 9(6)	0.124 2(4)	−0.136 1(7)	0.134 8(6)	0.288 9(3)	0.485 4(6)
C(31)	0.285 1(11)	0.140 4(6)	−0.119 7(12)	0.203 6(10)	0.246 9(6)	0.562 2(12)
H(31A)	0.311(—)	0.169(—)	−0.051(—)	0.269(—)	0.263(—)	0.570(—)
H(31B)	0.325(—)	0.101(—)	−0.101(—)	0.203(—)	0.246(—)	0.640(—)
H(31C)	0.299(—)	0.162(—)	−0.184(—)	0.205(—)	0.202(—)	0.536(—)
C(4)	0.185 8(8)	0.028 1(5)	−0.026 6(9)	0.108 8(8)	0.370 4(5)	0.615 1(9)
O(4)	0.221 5(5)	−0.005 5(4)	−0.102 1(6)	0.082 5(5)	0.320 2(3)	0.673 0(6)
C(41)	0.147 2(9)	−0.035 2(6)	−0.204 5(10)	−0.017 3(10)	0.304 7(6)	0.628 5(11)
H(41A)	0.110(—)	−0.065(—)	−0.179(—)	−0.054(—)	0.344(—)	0.635(—)
H(41B)	0.105(—)	−0.002(—)	−0.252(—)	−0.040(—)	0.294(—)	0.545(—)
H(41C)	0.170(—)	−0.058(—)	−0.260(—)	−0.040(—)	0.271(—)	0.669(—)
C(5)	0.164 4(7)	−0.004 1(5)	0.066 2(9)	0.110 2(7)	0.437 1(5)	0.650 6(9)
C(6)	0.174 4(7)	−0.074 1(5)	0.088 9(9)	0.084 9(8)	0.459 3(5)	0.750 8(9)
O(6)	0.212 6(6)	−0.108 9(4)	0.019 8(6)	0.059 8(6)	0.410 9(4)	0.813 2(6)
C(61)	0.225 7(9)	−0.177 7(5)	0.042 2(11)	0.044 3(10)	0.430 0(6)	0.919 8(11)
H(61A)	0.084(—)	−0.185(—)	0.121(—)	0.102(—)	0.451(—)	0.975(—)
H(61B)	0.163(—)	−0.197(—)	0.028(—)	−0.006(—)	0.464(—)	0.900(—)
H(61C)	0.251(—)	−0.202(—)	−0.010(—)	0.027(—)	0.399(—)	0.967(—)
C(7)	0.149 7(8)	−0.102 1(5)	0.178 0(9)	0.087 9(7)	0.525 2(5)	0.779 5(9)
H(7)	0.158(—)	−0.150(—)	0.191(—)	0.072(—)	0.539(—)	0.849(—)
C(8)	0.112 8(7)	−0.062 9(5)	0.248 3(9)	0.115 3(7)	0.570 2(5)	0.710 2(10)
C(81)	0.085 2(7)	−0.098 7(5)	0.339 7(9)	0.118 5(8)	0.642 7(5)	0.745 8(9)
O(81)	0.094 8(6)	−0.156 1(3)	0.358 3(7)	0.095 4(6)	0.660 3(4)	0.828 8(7)
O(82)	0.046 2(5)	−0.059 5(3)	0.400 8(6)	0.146 4(6)	0.680 1(3)	0.676 4(7)
C(82)	0.012 2(10)	−0.092 6(6)	0.485 4(11)	0.152 5(11)	0.748 4(5)	0.704 3(13)
H(82A)	−0.037(—)	−0.124(—)	0.447(—)	0.090(—)	0.766(—)	0.699(—)
H(82B)	0.064(—)	−0.115(—)	0.546(—)	0.197(—)	0.758(—)	0.783(—)
H(82C)	−0.016(—)	−0.065(—)	0.534(—)	0.172(—)	0.780(—)	0.652(—)
C(9)	0.105 8(7)	0.003 0(5)	0.236 3(9)	0.141 3(7)	0.552 4(5)	0.616 2(9)
H(9)	0.087(—)	0.029(—)	0.293(—)	0.160(—)	0.586(—)	0.570(—)
C(10)	0.129 6(8)	0.033 1(5)	0.142 6(10)	0.140 3(8)	0.485 2(5)	0.587 2(9)

arising from packing or stacking in the crystal lattice. Values are tabulated up to a limit of 3.7 Å for contacts of this type [together with type (i) contacts] in Tables 7—12. Again, contacts of this type may not necessarily carry the implication of causality if observed, but may simply be indicative of suitable positioning of adjacent molecular fragments for interaction once the process has been initiated by some other mechanism involving, *e.g.* C–I bond cleavage. In fact, a considerable number of interactions of this type are observed and are depicted in the Figures for those examples where significant non-peripheral overlap is found; also evident from these Figures in many cases, is the interaction between large adjacent substituents about the naphthalene skeleton periphery. Table 13, of atomic deviations of the substituent atoms from the skeletal plane, quantifies these deviations.

Individual features of the various structures are now examined in more detail, together with that of (1).

Compound (1).—The unit cell of (1) is $P2_1/c$ with a = 10.294(5), b = 18.868(9), c = 7.549(6), β = 90.29(5)°, Z = 4. Thus the asymmetric unit of the structure is one molecule. This exhibits a close iodine contact to a near neighbour [I · · · I ($\bar{x}$, $\bar{y}$, $1 - z$) 4.148(2) Å, and overlaps another symmetry-related neighbour (x, $\frac{1}{2} - y$, $\frac{1}{2} + z$) (Table 7, Figure 2)]. The molecular plane lies approximately normal to the crystallographic c axis.

The methoxy-substituents at positions 4 and 6 have their CO skeletons closely coplanar with the naphthalene skeleton (Table 13), the two methyl groups being directed away from each other. The 2-methoxy-group is likewise coplanar with the methyl directed away from the iodine; as usual, for all coplanar methoxy-groups the exocyclic angles to the naphthalene skeleton are unsymmetrical being enlarged on the side enclosed by the methyl group as a consequence of methyl hydrogen–adjacent aromatic hydrogen interactions. The carboxylate group at position 8 is approximately coplanar with the ring system in (1), (6), (7), (11), and (12). In all compounds, the exocyclic angles at the iodine are unsymmetrical, again presumably because of interaction between the iodine and H(9).

Compound (7).—The asymmetric unit of this structure is similarly one independent molecule. A close I · · · I intermolecular contact is observed [Table 8, Figure 3(a)]. The molecules lie almost normal to the crystallographic a axis and overlap is observed between successive molecules generated by the unit a translation [Table 8,

TABLE 4

Atomic fractional cell co-ordinates for (11)

	Molecule 1			Molecule 2		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
I(1)	0.069 60(2)	0.406 83(5)	0.100 79(6)	0.050 34(2)	0.877 00(4)	1.179 20(6)
C(1)	0.178 9(3)	0.437 9(5)	0.149 6(7)	0.161 0(3)	0.906 7(5)	1.200 2(7)
C(2)	0.220 0(3)	0.360 6(5)	0.063 3(7)	0.190 5(3)	1.009 7(5)	1.314 4(8)
O(2)	0.188 1(2)	0.260 3(4)	−0.056 3(5)	0.148 8(2)	1.091 0(4)	1.395 9(5)
C(21)	0.178 9(5)	0.150 0(6)	−0.004 2(10)	0.156 1(4)	1.131 1(7)	1.568 2(9)
H(21A)	0.224(—)	0.133(—)	0.029(—)	0.148(—)	1.061(—)	1.612(—)
H(21B)	0.150(—)	0.159(—)	0.087(—)	0.205(—)	1.167(—)	1.599(—)
H(21C)	0.158(—)	0.080(—)	−0.085(—)	0.128(—)	1.188(—)	1.628(—)
C(3)	0.292 5(3)	0.376 7(5)	0.088 8(7)	0.265 4(3)	1.035 7(5)	1.334 9(7)
O(3)	0.335 2(2)	0.297 5(4)	0.005 3(5)	0.296 6(2)	1.136 8(3)	1.448 9(5)
C(31)	0.332 0(5)	0.276 5(9)	−0.169 3(9)	0.303 6(4)	1.243 9(6)	1.392 5(9)
H(31A)	0.285(—)	0.250(—)	−0.209(—)	0.332(—)	1.234(—)	1.302(—)
H(31B)	0.345(—)	0.355(—)	−0.192(—)	0.258(—)	1.260(—)	1.364(—)
H(31C)	0.362(—)	0.224(—)	−0.228(—)	0.326(—)	1.316(—)	1.472(—)
C(4)	0.325 0(3)	0.470 9(5)	0.210 7(7)	0.372 2(3)	0.957 5(5)	1.245 1(8)
O(4)	0.396 3(2)	0.479 1(4)	0.248 3(5)	0.379 5(2)	0.992 9(4)	1.256 8(6)
C(41)	0.442 3(4)	0.521 2(8)	0.140 2(10)	0.414 5(5)	0.976 8(8)	1.399 7(12)
H(41A)	0.434(—)	0.470(—)	0.032(—)	0.395(—)	1.023(—)	1.496(—)
H(41B)	0.434(—)	0.602(—)	0.105(—)	0.406(—)	0.894(—)	1.403(—)
H(41C)	0.493(—)	0.529(—)	0.163(—)	0.464(—)	1.001(—)	1.411(—)
C(5)	0.284 9(3)	0.554 7(5)	0.310 5(7)	0.277 2(3)	0.849 4(5)	1.128 6(7)
C(6)	0.313 8(3)	0.654 9(5)	0.439 2(7)	0.316 8(3)	0.764 7(6)	1.032 6(8)
O(6)	0.387 1(2)	0.686 9(4)	0.462 9(5)	0.390 7(2)	0.777 8(4)	1.059 1(6)
C(61)	0.423 3(3)	0.633 5(6)	0.559 8(8)	0.430 4(4)	0.833 1(7)	0.957 3(13)
O(61)	0.395 8(2)	0.563 0(4)	0.627 2(6)	0.406 4(3)	0.870 6(6)	0.855 6(8)
C(62)	0.500 5(4)	0.675 2(7)	0.559 6(11)	0.508 3(4)	0.839 9(8)	1.004 7(14)
H(62A)	0.516(—)	0.662(—)	0.450(—)	0.509(—)	0.879(—)	1.117(—)
H(62B)	0.528(—)	0.630(—)	0.617(—)	0.512(—)	0.761(—)	0.999(—)
H(62C)	0.512(—)	0.760(—)	0.610(—)	0.545(—)	0.895(—)	0.943(—)
C(7)	0.272 8(3)	0.731 6(6)	0.529 5(8)	0.286 0(4)	0.665 1(6)	0.921 6(9)
H(7)	0.295(3)	0.788(5)	0.607(7)	0.319(3)	0.609(5)	0.860(8)
C(8)	0.199 7(3)	0.713 2(5)	0.499 7(7)	0.212 5(3)	0.644 4(5)	0.898 9(7)
C(81)	0.155 8(3)	0.797 9(5)	0.603 5(8)	0.180 7(3)	0.534 0(5)	0.773 2(8)
O(81)	0.179 7(3)	0.886 2(4)	0.703 9(6)	0.213 0(2)	0.454 3(4)	0.705 1(6)
O(82)	0.086 7(2)	0.763 2(4)	0.569 9(6)	0.111 7(2)	0.533 0(4)	0.741 5(5)
C(82)	0.040 3(4)	0.841 2(7)	0.661 4(10)	0.076 3(4)	0.428 7(7)	0.625 0(9)
H(82A)	0.048(—)	0.849(—)	0.773(—)	0.098(—)	0.420(—)	0.522(—)
H(82B)	0.049(—)	0.920(—)	0.641(—)	0.081(—)	0.357(—)	0.660(—)
H(82C)	−0.011(—)	0.817(—)	0.637(—)	0.026(—)	0.425(—)	0.598(—)
C(9)	0.169 5(3)	0.620 6(6)	0.375 7(8)	0.172 0(3)	0.721 0(5)	0.987 7(7)
H(9)	0.123(—)	0.615(—)	0.352(—)	0.121(3)	0.703(5)	0.969(7)
C(10)	0.209 7(3)	0.538 2(5)	0.278 5(7)	0.202 4(3)	0.826 1(5)	1.106 5(7)

TABLE 5

Atomic fractional cell co-ordinates for (10)

	Molecule 1			Molecule 2		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
I(1)	0.698 11(8)	0.496 4(2)	0.239 17(8)	0.427 55(8)	−0.090 8(2)	0.320 09(9)
C(1)	0.707 3(10)	0.409 3(23)	0.335 9(10)	0.542 0(10)	−0.141 4(25)	0.379 6(11)
C(2)	0.641 8(10)	0.395 4(30)	0.340 8(11)	0.580 1(10)	−0.113 9(24)	0.344 7(11)
O(2)	0.577 9(7)	0.448 8(19)	0.281 2(7)	0.550 2(8)	−0.044 9(21)	0.278 9(7)
C(21)	0.509 3(10)	0.431 5(34)	0.280 6(12)	0.587 9(14)	−0.038 5(38)	0.240 1(13)
H(21A)	0.468(—)	0.464(—)	0.237(—)	0.558(—)	0.012(—)	0.193(—)
H(21B)	0.509(—)	0.497(—)	0.318(—)	0.598(—)	−0.161(—)	0.229(—)
H(21C)	0.501(—)	0.307(—)	0.289(—)	0.633(—)	0.020(—)	0.262(—)
C(3)	0.644 0(9)	0.336 9(25)	0.403 7(9)	0.660 5(11)	−0.142 6(26)	0.380 7(11)
H(3)	0.597(—)	0.329(—)	0.405(—)	0.689(—)	−0.121(—)	0.357(—)
C(4)	0.709 8(8)	0.294 9(24)	0.460 8(10)	0.696 2(9)	−0.200 1(24)	0.451 5(10)
O(4)	0.713 9(6)	0.236 1(18)	0.522 8(7)	0.769 9(7)	−0.234 0(20)	0.485 3(7)
C(41)	0.645 8(10)	0.240 7(29)	0.525 8(11)	0.815 0(11)	−0.203 0(32)	0.454 8(13)
H(41A)	0.653(—)	0.202(—)	0.571(—)	0.866(—)	−0.239(—)	0.484(—)
H(41B)	0.608(—)	0.169(—)	0.490(—)	0.815(—)	−0.082(—)	0.443(—)
H(41C)	0.626(—)	0.360(—)	0.519(—)	0.796(—)	−0.270(—)	0.411(—)
C(5)	0.777 6(8)	0.301 8(23)	0.457 3(9)	0.653 6(9)	−0.224 3(23)	0.487 8(10)
C(6)	0.848 7(9)	0.256 6(25)	0.514 5(9)	0.686 2(10)	−0.283 5(24)	0.561 2(11)
O(6)	0.858 1(6)	0.201 2(17)	0.579 1(6)	0.763 4(7)	−0.297 4(17)	0.601 3(7)
C(61)	0.861 7(11)	0.340 6(31)	0.625 9(12)	0.805 4(12)	−0.143 2(32)	0.632 3(12)
H(61A)	0.869(—)	0.297(—)	0.671(—)	0.798(—)	−0.062(—)	0.596(—)
H(61B)	0.816(—)	0.410(—)	0.607(—)	0.859(—)	−0.170(—)	0.658(—)
H(61C)	0.902(—)	0.422(—)	0.636(—)	0.793(—)	−0.091(—)	0.665(—)
C(7)	0.912 2(9)	0.257 4(24)	0.507 7(10)	0.642 0(11)	−0.317 5(28)	0.592 4(11)
I(7)	1.013 54(8)	0.164 6(2)	0.590 38(8)	0.692 71(10)	−0.400 8(3)	0.696 06(9)
C(8)	0.910 0(10)	0.305 7(28)	0.443 0(10)	0.566 8(10)	−0.294 1(30)	0.553 6(11)
H(8)	0.955(—)	0.303(—)	0.439(—)	0.535(—)	−0.320(—)	0.575(—)
C(9)	0.841 6(10)	0.354 0(26)	0.388 4(10)	0.533 3(10)	−0.238 5(30)	0.484 9(10)
H(9)	0.838(—)	0.397(—)	0.344(—)	0.480(—)	−0.227(—)	0.459(—)
C(10)	0.774 7(10)	0.353 2(22)	0.391 9(9)	0.575 5(10)	−0.203 1(25)	0.451 1(10)

TABLE 6

Non-hydrogen molecular geometries. The geometry of (1) is included for comparison. The two values for compounds (10)—(12) are for molecules 1, 2 respectively

	(1)	(7)	(6)	(12)	(11)	(10)
Distances (Å)						
I(1)–C(1)	2.096(7)	2.091(4)	2.01(2)	2.09(1), 2.10(1)	2.087(6), 2.093(6)	2.11(2). 2.09(2)
C(1)–C(2)	1.364(10)	1.368(7)	1.34(2)	1.33(2), 1.39(1)	1.348(8). 1.384(7)	1.40(3), 1.34(4)
C(1)–C(10)	1.427(9)	1.421(6)	1.50(3)	1.44(1), 1.42(2)	1.437(7), 1.400(8)	1.39(2), 1.43(3)
C(2)–C(3)	1.405(10)	1.407(7)	1.37(4)	1.42(2), 1.41(2)	1.378(9), 1.421(9)	1.41(3), 1.46(3)
C(2)–O(2)	1.367(9)	1.363(5)	1.36(3)	1.40(1), 1.40(2)	1.401(6), 1.369(8)	1.38(2), 1.35(3)
O(2)–C(21)	1.425(10)	1.429(7)	1.46(2)	1.41(1), 1.43(1)	1.439(10), 1.427(9)	1.40(3), 1.39(4)
C(3)–C(4)	1.375(10)	1.365(7)	1.39(3)	1.38(2), 1.37(2)	1.375(10), 1.375(9)	1.35(2), 1.41(2)
C(3)–O(3)				1.36(2), 1.36(1)	1.372(8), 1.378(6)	
O(3)–C(31)				1.40(2), 1.39(1)	1.448(9), 1.425(9)	
C(4)–C(5)	1.418(9)	1.424(7)	1.44(3)	1.41(2), 1.42(1)	1.427(8), 1.432(7)	1.43(3), 1.44(4)
C(4)–O(4)	1.359(8)	1.365(6)	1.37(3)	1.38(2), 1.37(1)	1.378(7), 1.385(8)	1.38(3), 1.35(2)
O(4)–C(41)	1.436(10)	1.421(8)	1.44(3)	1.45(1), 1.42(2)	1.417(10), 1.442(12)	1.43(3) 1.39(3)
C(5)–C(6)	1.446(10)	1.432(6)	1.44(3)	1.45(1), 1.45(2)	1.425(7), 1.414(9)	1.42(2), 1.46(3)
C(5)–C(10)	1.435(9)	1.439(6)	1.38(3)	1.42(2), 1.41(2)	1.436(8), 1.419(8)	1.44(3), 1.41(2)
C(6)–C(7)	1.363(10)	1.357(7)	1.36(4)	1.37(2), 1.38(1)	1.356(9), 1.352(8)	1.38(3), 1.39(4)
C(6)–O(6)	1.347(8)	1.359(6)	1.40(3)	1.36(1), 1.36(1)	1.398(7), 1.408(8)	1.38(3), 1.39(2)
O(4) · · · O(6)	2.536(7)	2.560(5)	2.60(2)	2.59(1), 2.59(1)	2.654(6), 2.663(6)	2.61(2), 2.62(2)
O(6)–C(61)	1.430(10)		1.30(3)	1.43(1), 1.42(2)	1.369(9), 1.386(11)	1.44(3), 1.41(3)
C(61)–O(61)			1.33(3)		1.187(9), 1.171(13)	
C(61)–C(62)			1.35(4)		1.491(10), 1.519(12)	
C(7)–C(8)	1.416(10)	1.402(7)	1.43(4)	1.40(2), 1.39(2)	1.393(9), 1.394(9)	1.42(3), 1.36(3)
C(7)–I(7)						2.10(2), 2.06(2)
C(8)–C(9)	1.377(10)	1.372(7)	1.36(3)	1.35(1), 1.36(2)	1.362(8), 1.344(9)	1.37(2), 1.36(3)
C(8)–C(81)	1.495(10)	1.495(7)	1.47(3)	1.48(2), 1.53(1)	1.495(9), 1.497(8)	
C(81)–O(81)	1.184(9)	1.195(7)	1.17(3)	1.19(1), 1.21(2)	1.189(7), 1.202(8)	
C(81)–O(82)	1.345(9)	1.334(6)	1.33(3)	1.34(1), 1.30(1)	1.334(8), 1.335(8)	
O(82)–C(82)	1.448(12)	1.448(8)	1.44(3)	1.45(2), 1.43(1)	1.440(9), 1.438(8)	
C(9)–C(10)	1.416(10)	1.411(7)	1.43(3)	1.42(2), 1.41(1)	1.409(9), 1.423(7)	1.41(3), 1.40(4)
Angles (°)						
I(1)–C(1)–C(2)	117.0(5)	117.6(3)	122(2)	116.5(8), 116.3(10)	119.5(4), 115.8(4)	118(1), 114(1)
I(1)–C(1)–C(10)	122.2(5)	121.0(3)	123(2)	122.5(9), 122.1(7)	120.2(4), 122.0(4)	122(2), 122(2)
C(2)–C(1)–C(10)	120.7(6)	121.4(4)	114(2)	121.1(11), 121.6(11)	120.3(5), 122.1(5)	120(2), 124(2)
C(1)–C(2)–C(3)	119.8(7)	120.3(4)	126(2)	121.4(10), 119.1(11)	122.2(5), 118.9(6)	121(2), 120(2)
C(1)–C(2)–O(2)	117.8(6)	117.5(4)	116(2)	122.6(11), 120.8(11)	119.0(5), 120.6(6)	115(2), 124(2)
O(2)–C(2)–C(3)	122.4(6)	122.2(4)	118(2)	115.9(11), 120.1(9)	118.8(5), 120.3(5)	124(2), 116(2)
C(2)–O(2)–C(21)	119.1(6)	118.8(4)	122(2)	115.4(8). 115.2(9)	113.6(5), 119.9(6)	118(2), 123(2)
C(2)–C(3)–C(4)	121.1(7)	120.2(5)	120(2)	119.3(11), 120.3(9)	120.1(5), 120.0(5)	120(2), 119(2)
C(2)–C(3)–O(3)					123.1(5), 120.4(5)	
O(3)–C(2)–C(4)					116.6(5), 119.5(6)	
C(3)–O(3)–C(31)					116.8(8), 113.5(5)	
C(3)–C(4)–C(5)	121.3(6)	121.7(4)	118(2)	120.8(11), 121.3(10)	121.0(5), 121.6(6)	121(2), 120(2)
C(3)–C(4)–O(4)	121.4(6)	122.7(4)	124(2)	117.5(11), 115.8(9)	120.0(5), 117.8(5)	122(2), 120(2)
O(4)–C(4)–C(5)	117.3(6)	115.5(4)	118(2)	121.7(9), 122.9(11)	118.7(5), 120.2(5)	117(1), 120(2)
C(4)–O(4)–C(41)	118.4(6)	119.6(4)	119(2)	113.4(9), 115.4(8)	115.9(6). 113.9(6)	116(1), 123(2)
C(4)–C(5)–C(6)	125.2(6)	124.1(4)	121(2)	124.4(11), 124.4(10)	125.0(5), 124.7(5)	124(2), 123(2)
C(4)–C(5)–C(10)	117.2(6)	117.9(4)	120(2)	119.3(10), 118.7(11)	117.9(4), 117.8(5)	119(1), 120(2)
C(6)–C(5)–C(10)	117.6(6)	118.0(4)	119(2)	116.3(10), 116.9(9)	117.0(5), 117.5(5)	117(2), 116(2)
C(5)–C(6)–C(7)	120.5(6)	121.1(4)	119(2)	121.2(11), 120.8(11)	122.2(5), 122.5(6)	122(2), 121(2)
C(5)–C(6)–O(6)	117.2(6)	121.9(4)	125(2)	116.1(10), 115.1(9)	120.3(5), 119.9(5)	122(2), 119(2)
O(6)–C(6)–C(7)	122.3(6)	116.9(4)	116(2)	122.7(9), 124.0(11)	117.0(5), 117.5(6)	116(1), 120(2)
C(6)–O(6)–C(61)	118.9(6)		127(2)	117.5(10), 116.8(9)	118.4(5), 116.7(6)	115(2), 119(1)
O(6)–C(61)–C(62)			120(2)		109.1(6), 108.7(8)	
O(6)–C(61)–O(61)			113(2)		123.5(6), 124.4(7)	
O(61)–C(61)–C(62)			127(2)		127.4(7), 126.9(9)	
C(6)–C(7)–C(8)	121.1(7)	120.6(4)	122(2)	119.8(9), 119.1(11)	120.2(5), 119.4(6)	122(1), 119(2)
C(6)–C(7)–I(7)						120(1), 119(1)
C(8)–C(7)–I(7)						118(1), 122(2)
C(7)–C(8)–C(81)	118.4(6)	121.2(4)	119(2)	115.3(9). 117.4(11)	119.0(5), 117.7(5)	
C(7)–C(8)–C(9)	120.5(6)	120.5(4)	117(2)	122.3(11), 122.9(9)	119.9(6), 120.9(5)	116(2), 122(2)
C(81)–C(8)–C(9)	121.1(6)	118.3(4)	123(2)	122.4(11), 119.7(10)	121.1(6), 121.5(5)	
C(8)–C(81)–O(81)	125.7(7)	124.2(5)	124(2)	125.0(11), 121.4(11)	124.0(6), 124.5(6)	
C(8)–C(81)–O(82)	111.4(6)	111.9(4)	112(2)	113.0(9), 112.1(10)	112.2(5), 112.9(5)	
O(81)–C(81)–O(82)	122.8(7)	123.9(5)	124(2)	122.0(11). 126.5(10)	123.8(6), 122.5(5)	
C(81)–O(82)–C(82)	115.2(6)	115.1(4)	117(2)	115.2(9). 115.8(11)	116.1(5), 116.8(5)	
C(8)–C(9)–C(10)	120.1(6)	121.1(4)	123(2)	118.7(10), 118.6(10)	122.0(6), 121.3(6)	125(2), 121(2)
C(9)–C(10)–C(1)	119.9(6)	122.8(4)	120(2)	120.2(11). 119.5(10)	123.1(5), 122.0(5)	122(2), 122(2
C(9)–C(10)–C(5)	120.3(6)	118.7(4)	119(2)	121.6(9), 121.6(11)	118.5(5), 118.4(5)	118(1), 120(2)
C(1)–C(10)–C(5)	119.8(6)	118.5(4)	121(2)	118.2(11), 118.9(9)	118.4(5), 119.6(5)	119(2), 118(2)

Table 7

Intermolecular non-hydrogen contacts for (1) (These values were not recorded in ref. 1)

Atoms	Distance (Å)	Atoms	Distance (Å)
(i) Iodine–iodine contacts <4.5 Å			
I ··· I^{i}	2.148(2)		
(ii) Molecular overlap contacts <3.7 Å (as in Figure 2)			
C(2) ··· C(4^{ii})	3.538(11)	C(1) ··· O(6^{ii})	3.640(9)
C(3) ··· C(4^{ii})	3.660(10)	C(9) ··· C(61^{ii})	3.647(13)
O(2) ··· O(4^{ii})	3.585(8)	C(5) ··· C(7^{ii})	3.683(10)
O(2) ··· C(41^{ii})	3.522(13)	C(6) ··· C(8^{ii})	3.528(11)
C(4) ··· C(5^{ii})	3.701(10)	O(6) ··· C(8^{ii})	3.673(9)
C(5) ··· C(6^{ii})	3.696(10)	C(61) ··· C(81^{ii})	3.677(13)
C(10) ··· C(6^{ii})	3.495(10)	C(4) ··· C(10^{ii})	3.607(10)
C(10) ··· O(6^{ii})	3.625(9)		
(iii) Other contacts <3.5 Å			
O(81) ··· C(21^{iii})	3.148(11)	O(4) ··· C(82^{iv})	3.453(12)

Transformation of the asymmetric unit: i ($\bar{x}.\bar{y}$, $1 - z$), ii (x. $\frac{1}{2} - y$. $\frac{1}{2} + z$), iii ($1 + x$. $\frac{1}{2} - y$, $z - \frac{1}{2}$), iv ($1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$).

Table 8

Intermolecular non-hydrogen contacts for (7)

Atoms	Distance (Å)	Atoms	Distance (Å)
(i) Iodine–iodine contacts <4.5 Å			
I ··· I^{i}	3.687(1)		
(ii) Molecular overlap contacts <3.8 Å [as in Figure 3(b)]			
C(8) ··· C(1^{ii})	3.640(7)	O(6) ··· O(4^{ii})	3.706(6)
C(9) ··· C(2^{ii})	3.559(7)	O(6) ··· C(41^{ii})	3.702(9)
C(1) ··· C(21^{ii})	3.509(8)	O(82) ··· C(8^{ii})	3.659(7)
C(10) ··· O(2^{ii})	3.626(6)	C(82) ··· C(8^{ii})	3.511(9)
C(2) ··· C(21^{ii})	3.697(8)	C(82) ··· C(81^{ii})	3.667(9)
C(10) ··· C(21^{ii})	3.697(8)	O(82) ··· C(9^{ii})	3.539(7)
C(6) ··· C(3^{ii})	3.641(7)	C(82) ··· C(9^{ii})	3.680(9)
C(6) ··· C(4^{ii})	3.703(7)	C(81) ··· C(10^{ii})	3.622(7)
C(7) ··· C(4^{ii})	3.566(7)	O(82) ··· C(10^{ii})	3.630(6)
(iii) Other contacts <3.5 Å			
O(6) ··· C(21^{iii})	3.315(7)	O(4) ··· O(2^{iv})	3.469(5)
O(6) ··· O(2^{iv})	3.162(5)	O(6) ··· C(21^{iv})	3.442(8)

Transformation of the asymmetric unit: i ($\bar{x},\bar{y},\bar{z}$), ii ($1 + x$, y,z), iii ($1\frac{1}{2} + x$. $\frac{1}{2} - y$, $\frac{1}{2} + z$), iv ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$).

Table 9

Intermolecular non-hydrogen contacts for (6)

Atoms	Distance (Å)	Atoms	Distance (Å)
(i) Iodine–iodine contacts <4.5 Å			
I ··· I^{i}	4.305(3)		
(ii) Molecular overlap contacts <3.7 Å [as in Figure 4(b)]			
C(2) ··· C(3^{ii})	3.64(3)	O(62) ··· C(21^{ii})	3.29(4)
C(5) ··· C(21^{ii})	3.68(3)		
(iii) Molecular overlap contacts <3.7 Å [as in Figure 4(c)]			
C(41) ··· C(1^{iii})	3.70(3)	C(4) ··· C(3^{iii})	3.65(3)
O(4) ··· C(2^{iii})	3.60(3)	O(4) ··· C(3^{iii})	3.42(3)
C(41) ··· C(2^{iii})	3.52(3)	C(41) ··· C(3^{iii})	3.64(3)
O(61) ··· O(21^{iii})	3.50(3)		
(iv) Molecular overlap contacts <3.7 Å [as in Figure 4(d)]			
O(81) ··· C(6^{iv})	3.71(3)	C(81) ··· C(7^{iv})	3.59(4)
O(62) ··· O(61^{iv})	3.49(2)	C(81) ··· C(8^{iv})	3.67(3)
O(62) ··· C(61^{iv})	3.57(3)	O(82) ··· C(8^{iv})	3.69(3)
O(62) ··· C(62^{iv})	3.28(3)	C(9) ··· O(81^{iv})	3.56(3)
C(8) ··· C(7^{iv})	3.60(4)		
(v) Other contacts <3.5 Å			
O(81) ··· C(41^{v})	3.47(3)		

Transformation of the asymmetric unit: i ($1 - x$, $\bar{y},\bar{z}$), ii ($1 - x$. $\bar{y}$, $1 - z$), iii ($\bar{x}.\bar{y}$, $1 - z$). iv ($\frac{1}{2} + x$, $\frac{1}{2} - y$. z), v ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $1 - z$).

Table 10

Intermolecular non-hydrogen contacts for (12). Atoms derived from molecule 2 are italicized

Atoms	Distance (Å)	Atoms	Distance (Å)
(i) Iodine–iodine contacts <4.5 Å			
Nil			
(ii) Molecular overlap contacts <3.7 Å [as in Figure 5(b)]			
C(8) ··· *C(1^{i})*	3.64(1)	C(61) ··· *O(6^{i})*	3.53(1)
C(81) ··· *C(2^{i})*	3.53(1)	O(4) ··· *C(61^{i})*	3.63(1)
O(81) ··· *C(2^{i})*	3.55(1)	O(6) ··· *C(61^{i})*	3.52(2)
C(81) ··· *O(2^{i})*	3.70(1)	C(4) ··· *C(7^{i})*	3.59(1)
O(81) ··· *O(2^{i})*	3.55(1)	C(5) ··· C(7^{i})	3.53(1)
O(81) ··· *C(3^{i})*	3.69(1)	C(10) ··· *C(8^{i})*	3.65(1)
O(81) ··· *C(31^{i})*	3.43(2)	C(1) ··· *C(81^{i})*	3.70(1)
C(7) ·· *C(4)*^{i}	3.60(1)	C(2) ··· *C(81^{i})*	3.57(1)
C(61) ··· *O(4^{i})*	3.56(1)	C(2) ··· *O(81^{i})*	3.69(1)
C(6) ··· *C(5^{i})*	3.58(1)	C(3) ··· *C(81^{i})*	3.70(1)
C(7) ··· *C(5^{i})*	3.51(1)	C(31) ··· *O(81^{i})*	3.30(1)
C(5) ··· *C(6^{i})*	3.66(1)	C(9) ··· *C(9^{i})*	3.68(1)
C(6) ··· *C(6^{i})*	3.47(1)	C(10) ··· *(9^{i})*	3.60(1)
O(6) ··· *C(6^{i})*	3.54(1)	C(8) ··· *C(10^{i})*	3.62(1)
O(6) ··· *O(6^{i})*	3.28(1)	C(9) ··· *C(10^{i})*	3.62(1)
(iii) Other contacts <3.5 Å			
C(61) ··· O(2^{ii})	3.44(2)	*O(82)* ··· *C(41^{iii})*	3.46(1)
C(61) ··· C(21^{ii})	3.65(2)	*C(41)* ··· *O(81^{iv})*	3.26(2)
O(81) ··· *C(21^{iii})*	3.28(2)		

Transformation of the asymmetric unit: i ($\frac{1}{2} - x$, $y - \frac{1}{2}$, $1 - z$), ii ($\frac{1}{2} - x, y - \frac{1}{2}, \bar{z}$), iii ($\bar{x}$, $1 - y$, $1 - z$), iv ($\bar{x},\bar{y}$, $1 - z$)

Table 11

Intermolecular non-hydrogen contacts for (11). Atoms derived from molecule 2 are italicized

Atoms	Distance (Å)	Atoms	Distance (Å)
(i) Iodine–iodine contacts <4.5 Å			
I ··· I^{i}	3.961(2)	I ··· I^{ii}	4.202(2)
(ii) Molecular overlap contacts <3.7 Å [as in Figure 6(b)]			
O(61) ··· O(6)	3.474(8)	*C(81)* ··· C(8)	3.480(10)
O(61) ··· C(61)	3.278(9)	*O(82)* ··· C(8)	3.582(8)
C(61) ··· C(61)	3.582(11)	*C(8)* ··· C(81)	3.638(10)
C(61) ··· O(61)	3.620(9)	*O(82)* ··· C(81)	3.552(8)
O(61) ··· O(61)	3.571(7)	*C(9)* ··· C(81)	3.622(10)
C(7) ··· O(61)	3.381(9)	*C(9)* ··· O(81)	3.431(9)
O(81) ··· O(61)	3.691(7)	*C(91)* ··· O(81)	3.700(9)
O(61) ··· C(62)	3.606(10)	*C(8)* ··· O(81)	3.691(9)
C(61) ··· C(7)	3.646(9)	*O*(82) ··· O(82)	3.409(7)
C(7) ··· C(7)	3.627(11)	*O*(82) ··· C(9)	3.666(5)
C(8) ··· C(8)	3.698(10)		
(iii) Molecular overlap contacts <3.7 Å [as in Figure 6(c)]			
O(81) ··· O(2^{iii})	3.417(8)	*C(31)* ··· O(3^{iii})	3.562(10)
C(1) ··· C(21^{iii})	3 640(11)	*C(31)* ··· C(4^{iii})	3.347(11)
C(2) ··· C(21^{iii})	3.510(12)	*C(31)* ··· O(4^{iii})	3.546(9)
O(2) ··· C(21^{iii})	3.689(10)	*C(21)* ··· *O(81^{iii})*	3.632(8)
C(31) ··· C(3^{iii})	3.338(11)		
(iv) Molecular overlap contacts <3.7 Å [as in Figure 6(d)]			
C(8) ··· C(1^{iv})	3.588(10)	*O(81)* ··· C(31^{iv})	3.554(12)
C(81) ··· C(1^{iv})	3.651(10)	*O(6)* ··· C(41^{iv})	3.446(11)
C(81) ··· C(2^{iv})	3.667(10)	*C(41)* ··· O(6^{iv})	3.492(5)
O(81) ··· C(2^{iv})	3.494(9)	*C(21)* ··· O(81^{iv})	3.379(10)
O(81) ··· O(2^{iv})	3.381(7)	*C(91)* ··· C(9^{iv})	3.701(7)
(v) Other contacts <3.5 Å			
O(61) ··· *C(62^{v})*	3.436(10)	C(41) ··· C(41^{vii})	3.275(12)
O(4) ··· C(62^{vi})	3.448(11)		

Transformation of the asymmetric unit: i, ($\bar{x}$, $1 - y$, $1 - z$), ii ($\bar{x}$, $1 - y$, $\bar{z}$), iii (x, $1 + y$, $1 + z$), iv (x,y. $1 + z$), v ($1 - x$. $2 - y$, $2 - z$), vi ($1 - x$, $1 - y$, $1 - z$), vii ($1 - x$, $1 - y$, $1 - \bar{z}$).

TABLE 12

Intermolecular non-hydrogen contacts (10). Atoms derived from molecule 2 are italicized

Atoms	Distance (Å)	Atoms	Distance (Å)
(i) Iodine–iodine contacts <4.5 Å			
$\mathrm{I}(7)\cdots\mathrm{I}(7^{\mathrm{i}})$	4.435(3)	$I(7)\cdots I(1^{\mathrm{v}})$	4.224(4)
$I(7)\cdots I(1^{\mathrm{ii}})$	4.392(3)	$I(7)\cdots I(7^{\mathrm{vi}})$	4.477(3)
$I(7)\cdots I(1^{\mathrm{iii}})$	4.501(3)	$\mathrm{I}(1)\cdots\mathrm{I}(1^{\mathrm{vii}})$	4.264(3)
$\mathrm{I}(7)\cdots\mathrm{I}(1^{\mathrm{iv}})$	3.787(3)		
(ii) Molecular overlap contacts <3.7 Å [Figure 7(b)]			
$\mathrm{O}(2)\cdots C(2^{\mathrm{viii}})$	3.58(2)	$\mathrm{C}(10)\cdots C(41^{\mathrm{viii}})$	3.58(3)
$\mathrm{C}(2)\cdots C(3^{\mathrm{viii}})$	3.59(3)	$\mathrm{C}(41)\cdots C(6^{\mathrm{viii}})$	3.70(3)
$\mathrm{O}(2)\cdots C(3^{\mathrm{viii}})$	3.68(2)	$\mathrm{C}(61)\cdots O(6^{\mathrm{viii}})$	3.29(3)
$\mathrm{C}(3)\cdots C(4^{\mathrm{viii}})$	3.67(3)	$\mathrm{C}(41)\cdots\mathrm{C}(7^{\mathrm{viii}})$	3.66(3)
$\mathrm{C}(5)\cdots O(4^{\mathrm{viii}})$	3.59(2)		
(iii) Molecular overlap contacts <3.7 Å [Figure 7(c)]			
$\mathrm{C}(3)\cdots C(2)$	3.66(3)	$\mathrm{C}(6)\cdots C(41)$	3.67(3)
$\mathrm{C}(4)\cdots C(3)$	3.65(3)	$\mathrm{O}(4)\cdots C(5)$	3.66(2)
$\mathrm{C}(3)\cdots C(3)$	3.71(3)	$\mathrm{O}(4)\cdots C(61)$	3.62(3)
$\mathrm{O}(4)\cdots C(4)$	3.59(2)	$\mathrm{O}(6)\cdots C(61)$	3.24(3)
$\mathrm{O}(2)\cdots C(4)$	3.66(2)		

Transformations of the asymmetric unit: i $(2 - x, \bar{y}, 1 - z)$, ii $(1 - x, \bar{y}, 1 - z)$, iii $(1 - x, -1 - y, 1 - z)$, iv $(x + \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z)$, v $(\frac{1}{2} + x, -\frac{1}{2} - y, \frac{1}{2} + z)$, vi $(1\frac{1}{2} - x, \frac{1}{2} + y, 1\frac{1}{2} - z)$, vii $(1\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, viii $(x, 1 + y, z)$.

Figure 3(b)]. Location and refinement of the hydroxy-hydrogen H(6) shows it to be intramolecularly hydrogen-bonded to the neighbouring methoxy-oxygen O(4) [H(6) . . . O(4), 1.83(6) Å]. As in (1) all methoxy- and carboxy-substituents lie closely coplanar with the plane of the naphthalene ring skeleton; the disposition of the methoxy-methyl groups is also similar.

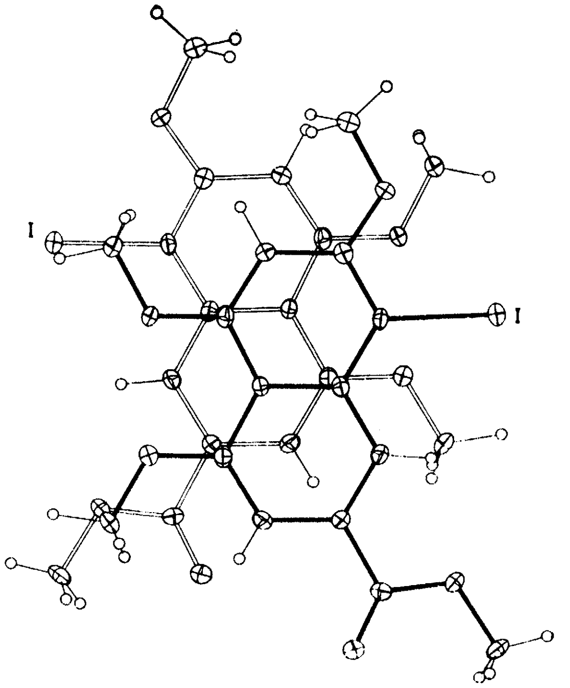

FIGURE 2 Projection of the parent molecule of (1) normal to the C_{10} naphthalene skeleton plane showing the disposition relative to the molecule generated by the symmetry transformation $(x, \frac{1}{2} - y, \frac{1}{2} + z)$. In this and subsequent similar projections the iodine atoms only are identified. Thermal ellipsoids in this and subsequent diagrams are at the 20% probability level, while associated hydrogen atoms have an arbitrary radius of 0.1 Å. A cell diagram for (1) is given in ref. 1

TABLE 13

Least squares planes through the molecules, defined by the C_{10} ring skeleton atoms are given in the form $pX + qY + rZ = s$ where the right hand orthogonal Å frame (X,Y,Z) is defined with X parallel to a, Z in the ac plane. σ (defining atoms) is in Å, as are the atom deviations. Also included are $\tau_{2,3,4}$, the torsion angles (°) C(3)–C(2)–O(2)–C(21), C(4)–C(3)–O(3)–C(31), C(3)–C(4)–O(4)–C(41), and θ, the dihedral angle between the C(8), O(81,82) plane and the ring plane. The two entries for (10)—(12) are for molecules 1, 2 respectively

	(1)	(7)	(6)	(12)	(11)	(10)
10^4p	3 551	6 988	8 949	7 633, 7 669	0 478, −0 220	−0 006, −0 253
10^4q	0 178	5 677	1 706	1 263, −0 970	5 777, 5 144	9 478, 9 516
10^4r	9 347	−4 353	4 124	6 336, 6 344	−8 149, −8 573	3 187, 3 064
s	3 242	0.844	2.824	2.099, 2.867	2.915, −1.394	4.896, 0.956
σ	0.02	0.004	0.04	0.02, 0.03	0.012, 0.014	0.03, 0.03
δI(1)	0.17	0.023	−0.31	0.13, 0.02	−0.020, −0.056	0.11, 0.10
δC(1)	0.02	0.004	−0.04	0.03, −0.01	0.009, −0.012	0.06, 0.04
δC(2)	−0.02	−0.005	−0.01	0.01, 0.05	−0.024, −0.014	−0.01, 0.00
δO(2)	−0.03	−0.014	−0.03	0.10, 0.17	−0.091, 0.074	0.02 0.12
δC(21)	−0.18	−0.042	0.03	−1.10, −1.04	−1.420, −0.860	−0.11, −0.09
δC(3)	−0.02	−0.002	0.07	−0.03, 0.00	0.005, 0.018	−0.05, −0.03
δO(3)				−0.13, −0.07	−0.062, 0.001	
δC(31)				1.05, 1.09	0.968, 1.290	
δC(4)	0.00	0.007	0.00	−0.02, −0.04	0.004, 0.015	−0.01, −0.03
δO(4)	0.00	−0.010	0.00	0.02, −0.02	−0.122, 0.191	−0.06, −0.11
δC(41)	−0.06	0.097	0.16	−1.29, −1.30	1.038, −1.002	−0.01, −0.10
δC(5)	0.01	−0.004	−0.01	0.01, −0.02	0.000, −0.007	0.02, 0.03
δC(6)	0.02	−0.003	−0.05	0.03, 0.02	0.000, −0.017	0.04, 0.03
δO(6)	0.04	−0.034	−0.16	0.11, 0.07	0.179, −0.134	0.03, 0.14
δC(61)	0.05		0.81	0.17, 0.25	−0.926, 1.048	1.31, 1.41
δC(7)	−0.01	0.001	0.02	0.01, 0.03	0.000, −0.009	0.00, 0.00
I(7)						−0.17, 0.00
δC(8)	−0.03	0.002	0.03	−0.04, 0.00	−0.018, 0.174	−0.04, −0.03
δC(81)	−0.04	−0.045	0.24	−0.10, 0.02	−0.047, 0.045	
δO(81)	−0.20	−0.211	0.44	−0.07, 0.04	0.043, −0.125	
δO(82)	0.15	0.099	0.08	−0.21, 0.01	−0.177, 0.297	
δC(9)	0.00	−0.004	0.02	0.00, −0.02	0.013, 0.013	−0.02, −0.02
δC(10)	0.03	0.005	−0.02	0.00, −0.01	0.011, −0.006	0.00, 0.01
τ_2	6.1	−1.0	0.0	78.5, 78.7	80.8, −56.3	−5.2, 14.7
τ_3				−84.5, −74.8	−126.1, 98.0	
τ_4	−1.2	−6.2	3.5	−97.0, −94.3	76.5, 79.6	−6.7, 4.6
θ	9.0	8.3	10.0	4.9, 0.8	5.4, 5.9	

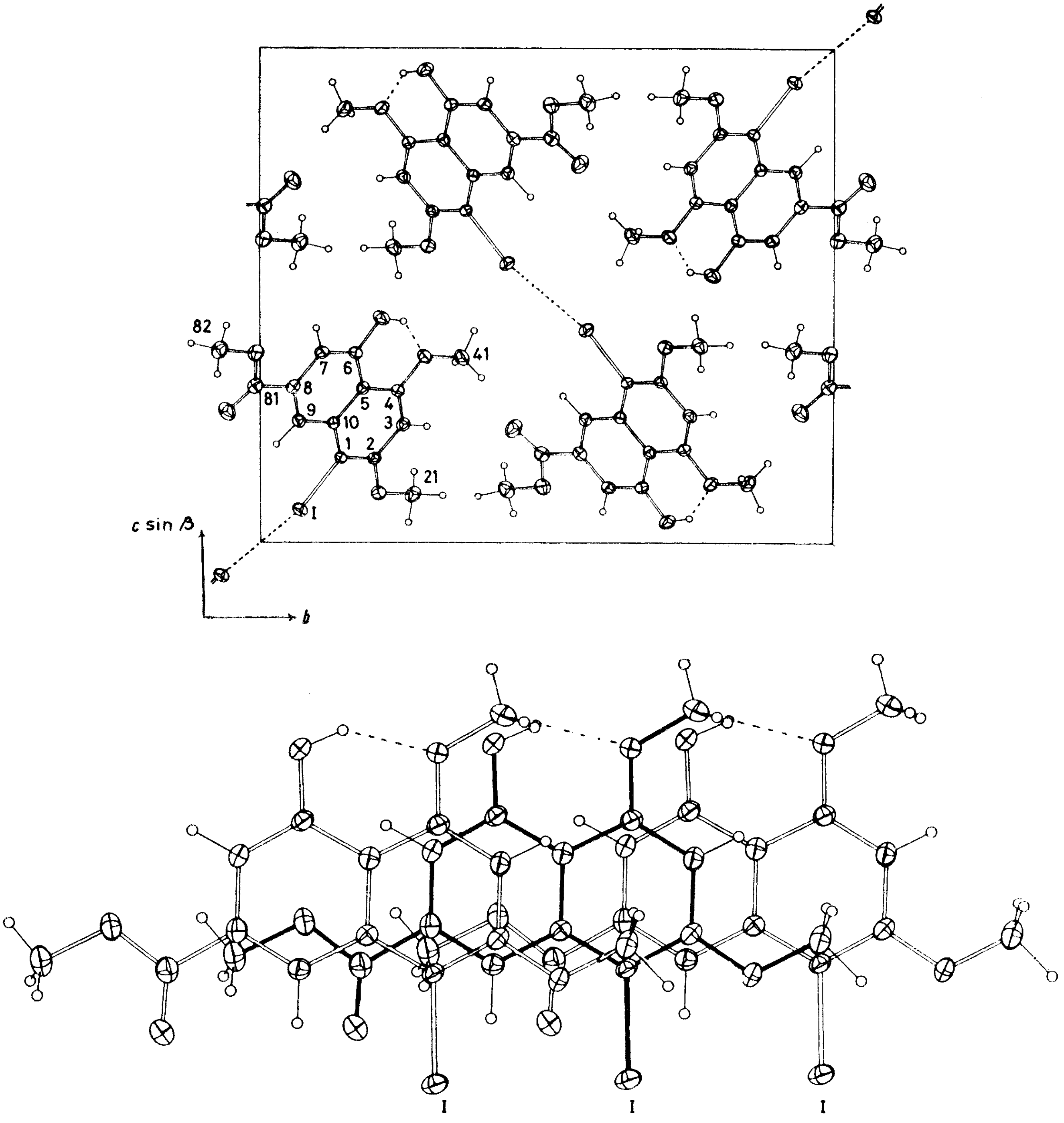

FIGURE 3 (a) Unit cell contents of (7) projected down *a*. (b) Projection of a single molecule as in Figure 2 with the nearest neighbours generated by unit *a* translations

Compound (6).—Here again the asymmetric unit of the structure is one independent molecule, again lying almost normal to crystallographic *a* (Figure 4). Although a number of close contacts between adjacent molecules displaced by $a/2$ are observed, the molecular overlaps involved are only peripheral. Close I ··· I contacts are observed [4.305(3) Å] (Figure 4) and in view of the pronounced layering of the molecules within the unit cell probably constitute the dominant van der Waals interaction normal to *c*. The methoxys are coplanar with the naphthalene skeleton with methyl dispositions as observed in (1) and (7). However, introduction of the acetoxy-group at position 6 introduces a new steric element over and above the 6-methoxy-group of (1) in that it is not possible for the acetoxy-species to lie within the naphthalene plane because of its bulk and it is thus constrained to be normal to that plane.

Compound (12).—The asymmetric unit for the structure comprises two independent molecules; these lie in pairs, the independent constituents of the pair being related by a pseudo-two-fold rotation [Figure 5(b)]. A considerable overlap between the two molecules is observed and in fact, is the only non-peripheral one found. Introduction of the methoxy-group at position **3** has profound implications for the disposition of the whole string C(2)—C(4), as the **3**-methoxy occupies the area of confrontation of the 2- and 4-methoxy groups in (1), (6), and (7). In consequence, the methyl groups of all three methoxy-groups of each molecule are disposed well out of the plane and such that those at the **2** and **4** position lie on the opposite side to that at the **3** position; the disposition of the 2-methoxy-group implies that it may be unable to be directed towards the neighbouring iodine and this in fact is found to be so also in (10) (see below). No close I • • • I contacts are found.

Compound (11).—The asymmetric unit again comprises two molecules, the planes of which lie approximately normal to *c*. Close I • • • I contacts are observed which are intercellular, similar to those found in (6). The disposition of the 2-, 3-, and 4-methoxy-groups in each

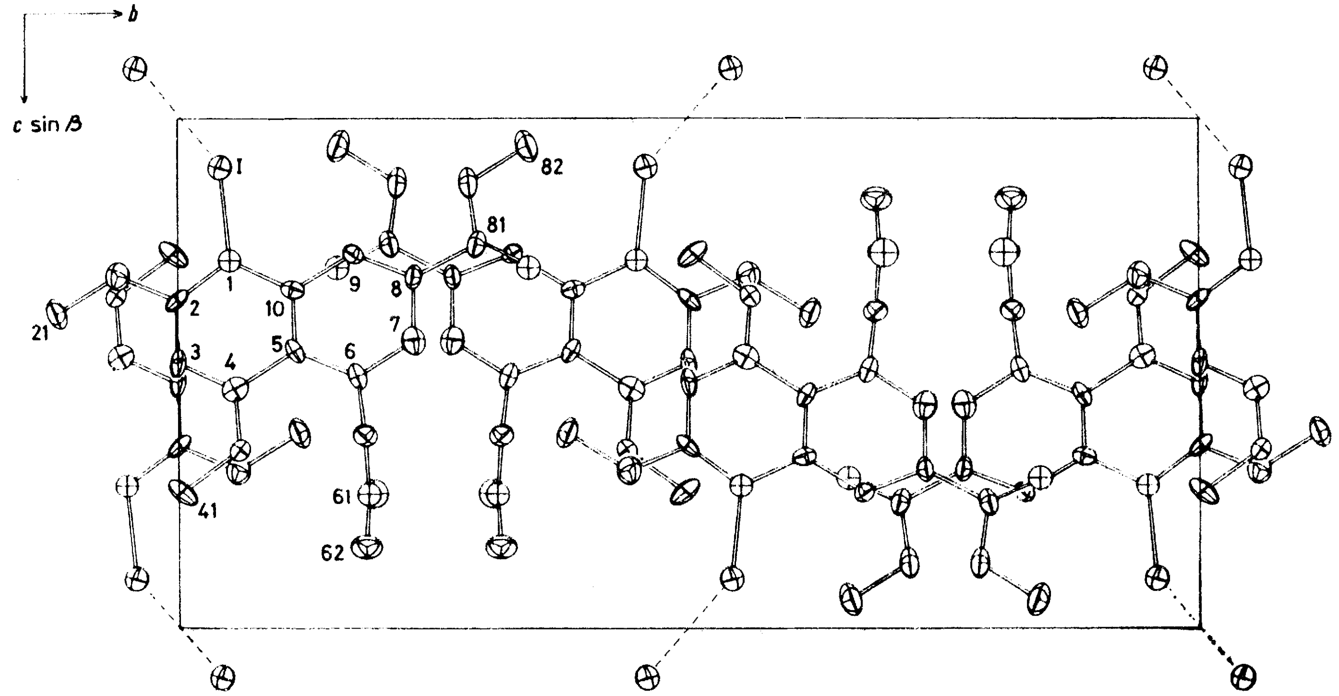

FIGURE 4 (a) Unit cell contents of (6) projected down *a*

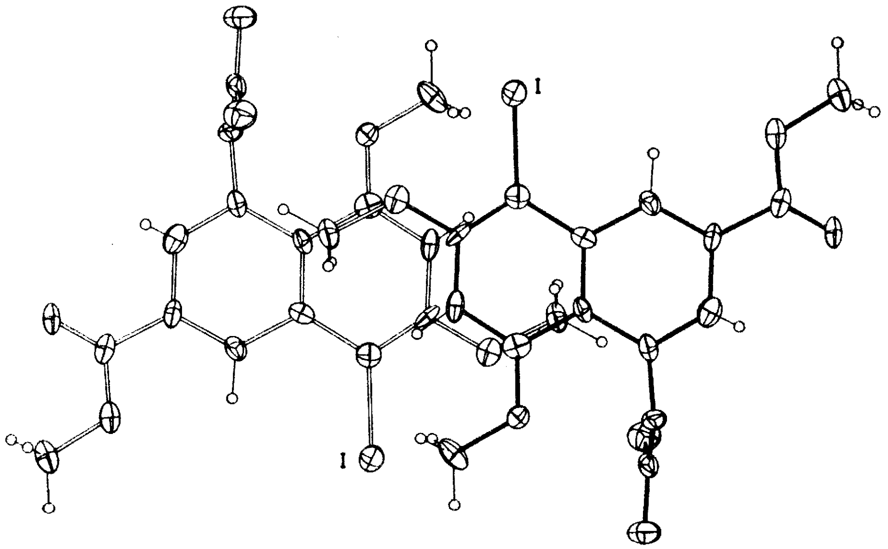

FIGURE 4 (b)

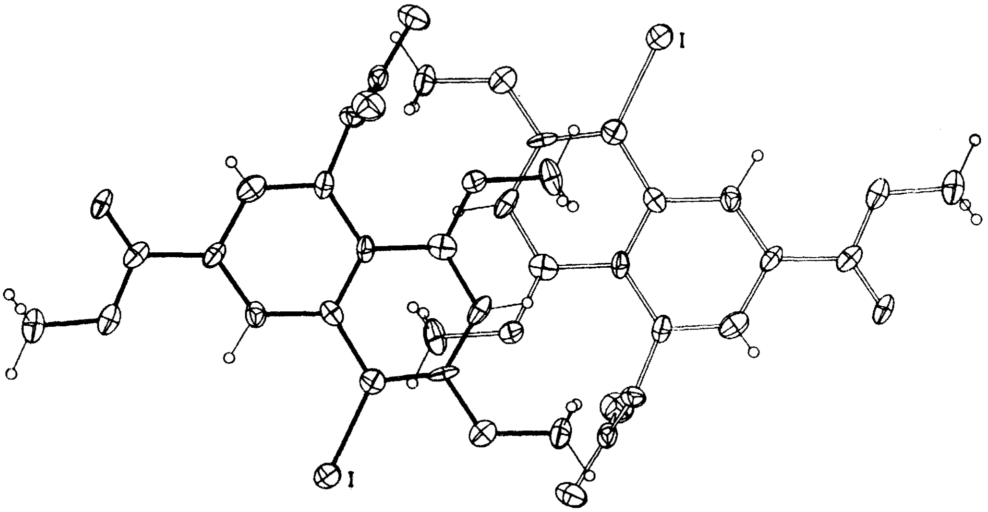

FIGURE 4 (c)

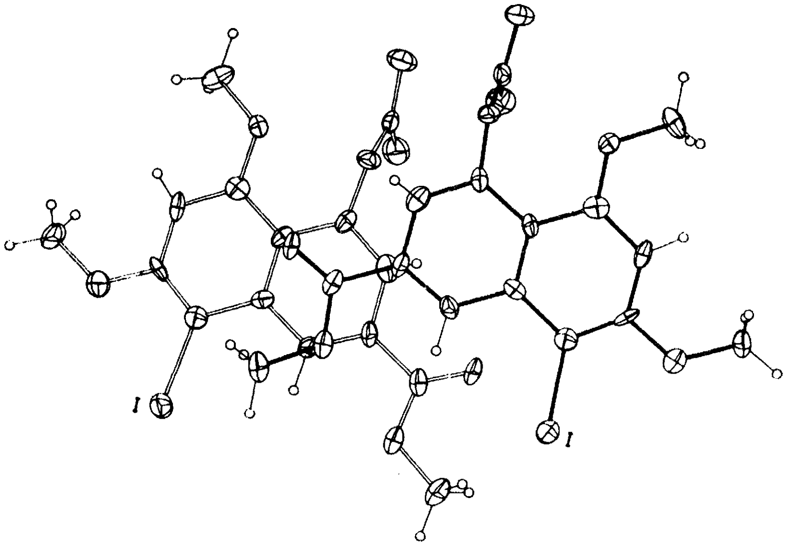

FIGURE 4 (d) [Figures 4(b)—(d) give projections of a single molecule together with nearest neighbours as given in Table 9]

molecule differ from those found in (12) in that the central 3-methoxy does not lie on the opposite side to the 2- and 4-methoxy-groups in molecule 1; rather the 3- and 4-groups are opposed to 2-methoxy. The 6-acetoxy group is disposed as in (6).

Compound (10).—Again we find the asymmetric unit to be a molecular pair related by a pseudo-two-fold rotation [*cf.* (12)]. (Note the non-conformity of the pair of 6-methoxy-groups, however!) A considerable number of I • • • I contacts are observed (doubtless, because the number of iodine atoms has doubled) (Table 12). While the 2- and 4-methoxy-groups are pseudo-coplanar with the naphthalene skeleton, 6-methoxy lies out of the plane, presumably because of the proximity of I(7). The following features may be noted generally about the molecular geometry, where the precision is sufficient to justify comment.

(i) Except in (6) where the precision is very bad, the aromatic C–I distances lie between 2.06(2) and 2.11(2) Å. The more precise values suggest 2.09—2.10 Å to be the norm in this type of compound.

(ii) Within the aromatic ring system bonds C(1)–C(2), C(3)–C(4), C(6)–C(7), and C(8)–C(9) are shorter than the remainder, the usual value being *ca.* 1.36 Å; the remaining bond lengths are generally greater than *ca.* 1.40 Å. Notable among the ring angles is the large exocyclic angle at C(5), typically *ca.* 124°, with correspondingly diminished endocyclic angles. Since in all cases C(4) and C(6) have oxygen atom substitutents it appears likely that the enlarged angle is a consequence of O(4) • • • O(6) repulsion, O • • • O typically being 2.6 Å. This repulsion, however, is insufficient, apparently, to drastically alter the exocyclic angles at C(6), distorted because of the methoxy-substituent, from their usual

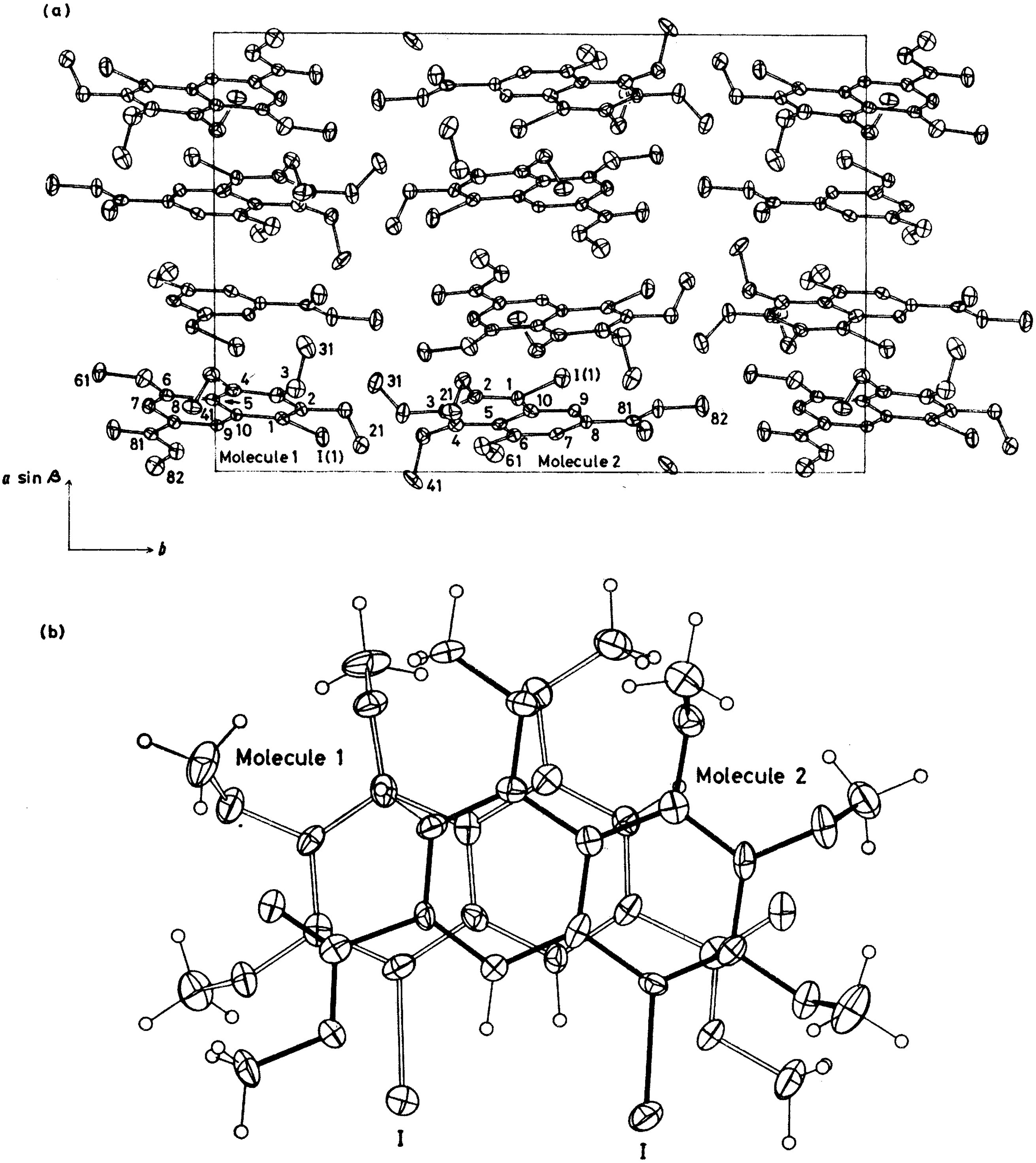

FIGURE 5 (a) Unit cell contents of (12) projected down c. (b) Projection of the two independent molecules of the asymmetric unit unsymmetrical values in those cases where the methoxymethyl is coplanar with the naphthalene skeleton.

(iii) In those examples [(11), (12)] where the 2-, 3-, and 4-methoxy-methyl groups are not coplanar with the naphthalene skeleton, no dramatic change in C–O distances is observed. There is a tendency, however, for the exocyclic angles about the naphthalene to become more symmetrical and it is also noticeable (Table 13) that the deviations of the oxygen atoms from the naphthalene skeleton plane become more pronounced, typically *ca.* 0.1 Å.

We now turn to consider the bearing of the above structural information on the question of thermal stability. Generally, there appears to be no detectable electronic substituent effect on the overall molecular bonding pattern, while, sterically, the crowding of the iodine differs little from one compound to the next. It further appears unlikely that intermolecular I . . . I contacts by themselves have much bearing on the problem since there is a variety of such contacts in both thermally sensitive and insensitive derivatives. Likewise, also, the question of charge-transfer overlap by itself appears not to be a prime determinant since it is found in both types of compound; in fact, although the overlaps found in (1) and (7) are greater, there is a notable tendency in (10)—(12) for pairwise packing to occur. The outstanding feature of compounds (6) and (10)—(12) in relation to (1) and (7) is the presence in the former of substituent groups which are non-coplanar with the naphthalene skeleton as a consequence of steric crowding of one sort or another; the non-hydrogen skeletons of (1) and (7) by contrast are closely coplanar. If therefore, one postulates iodine radical formation as an early step in the reaction process, it follows that the reaction will only be successful if it can proceed further by sliding of the moieties in the lattice relative to each other, and it is seen that in (6) and (10)—(12), the non-coplanar substituents constitute a gross impediment to such a process.

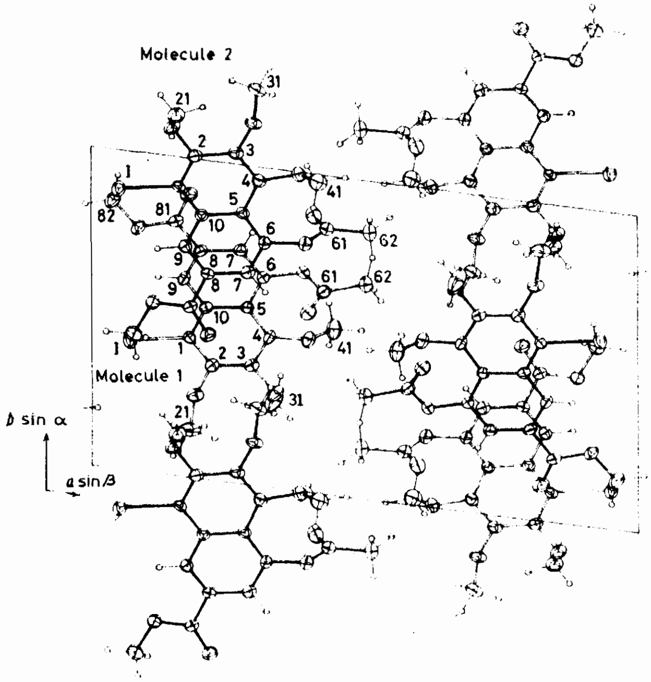

FIGURE 6 (a) Unit cell contents of (11) projected down *c*

The above study describes the structure determinations of six of the ten iodinated naphthalene derivatives prepared in this work. Of the remaining four, we note that (8) and (9) lose iodine readily on heating; their substituents are expected to be coplanar with the ring system and provide no impediment to dimerization by the above mechanism if we assume the molecules to pack in parallel arrays in the lattice. The other two, (4) and (5), which do not lose iodine readily have bulky substituents which might be expected to constitute an impediment to close approach or lateral displacement of

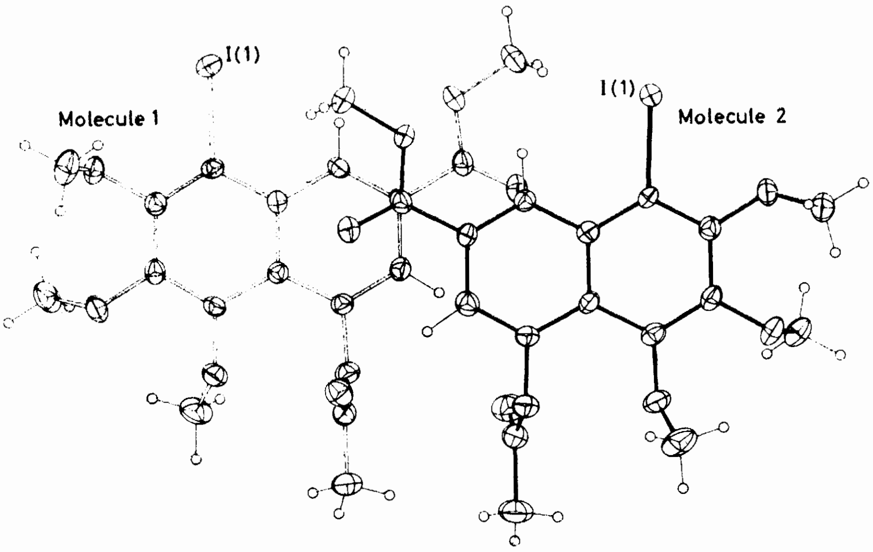

FIGURE 6 (b)

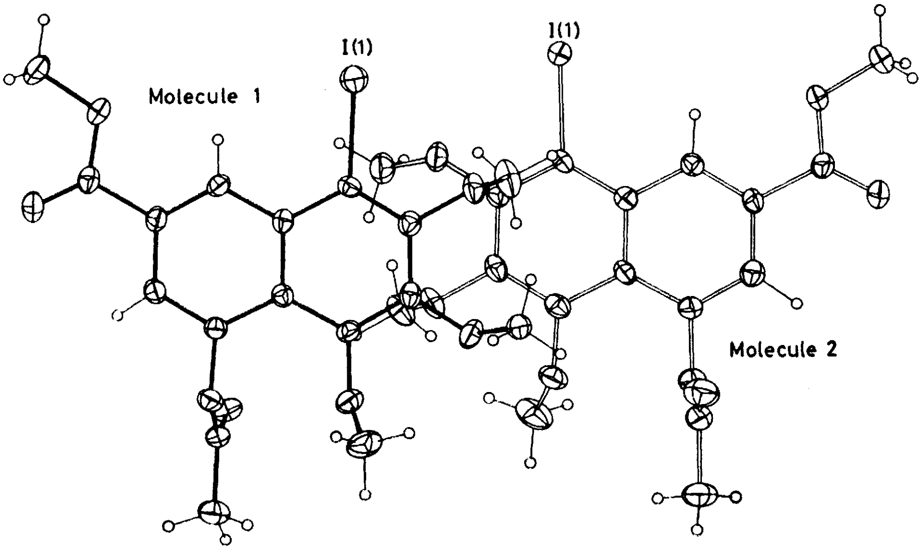

FIGURE 6 (c)

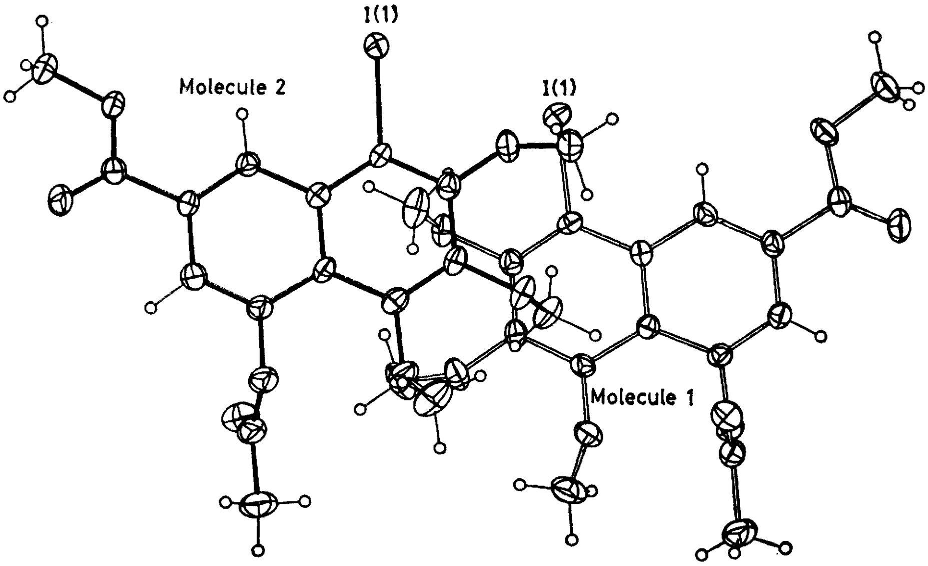

Figure 6 (d) [Figure 6(b)—(d) give projections of a single molecule together with nearest neighbours as given in Table 11]

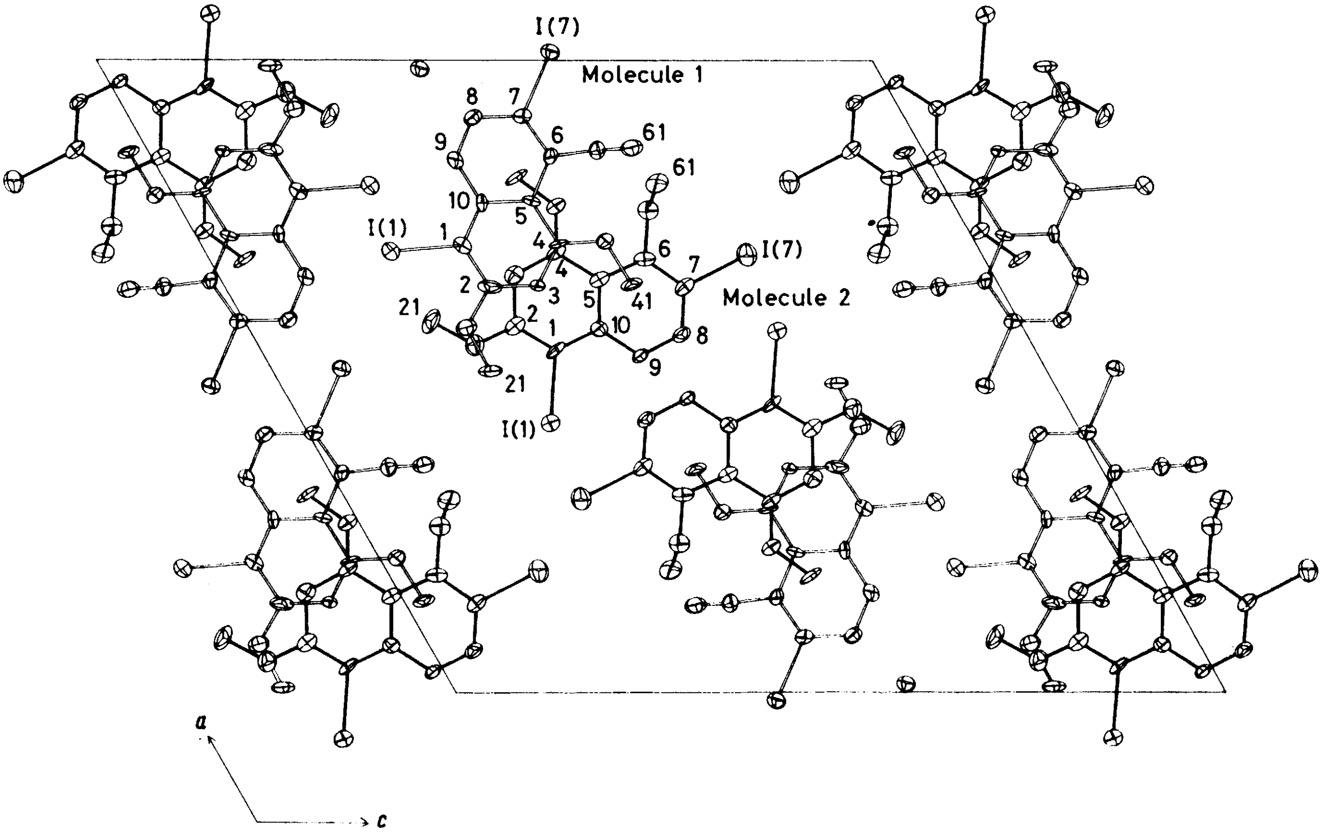

FIGURE 7 (a) Unit cell contents of (10) projected down *b*

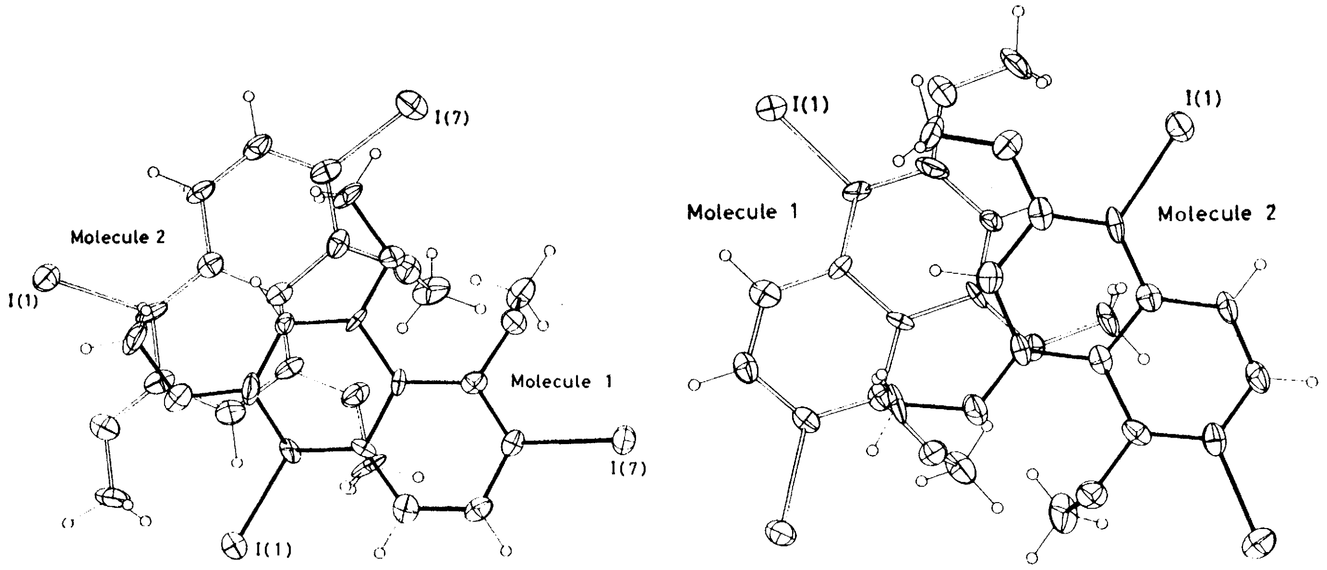

FIGURE 7 (b) [FIGURE 7 (c)
Molecular projections in Figures 7(b) and (c) as defined in Table 12]

the type expected to facilitate dimerization. At the phenomenological level, therefore, the observations within the whole series appear to be consistent with the proposed interpretation.

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