1,3-Benzoyl Migration of 2-Benzoyl-2-phenylazoindane-1,3-dione. Molecular Conformations and Crystal Structures of the Rearrangement Products, Indane-1,2,3-trione 2-(*N*-Benzoyl-*N*-phenylhydrazone) and Indane-1,2,3-trione 2-(*N*-Bromobenzoyl-*N*-phenylhydrazone)

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The solution and solid-state thermal rearrangement of 2-benzoyl- (4a) and 2-(*p*-bromobenzoyl)-2-phenylazoindane-1,3-dione (4b) have been studied. The expected product of the rearrangement of (4a), indane-1,2,3-trione 2-(*N*-phenylhydrazone) (6a) was found in high yield in the solution reaction, but only in trace amounts in the solid. The corresponding bromo-compound, indane-1,2,3-trione 2-(*N*-*p*-bromobenzoyl-*N*-phenylhydrazone) (6b) could only be detected in trace amounts in the solution rearrangement of (4b) and not at all in the solid-state rearrangement. To assign definitely the structure of this product of the solution rearrangement of (4a), crystal structures of both (6a) and (6b) were determined. Crystals of (6a) are monoclinic, with a = 6.774(2), b = 28.950(11), c = 9.018(3) Å, β = 96.08(1)°, space group $P2_1/c$; structure refined to R 0.063 on 2 951 non-zero reflections. Crystals of (6b) are triclinic, with a = 15.369(14), b = 13.917(17), c = 9.195(8) Å, α = 99.50(7), β = 85.12(7), and γ = 104.84(6)°, space group $P\bar{1}$, two molecules in the crystal asymmetric unit; structure refined R 0.081 on 4 425 non-zero reflections. The molecule of (6a), both when crystallized by itself and as a 1 : 1 complex with indane-1,2,3-trione 2-(*N*-phenylhydrazone), one of the molecules of (6b), and the *p*-t-butyl-derivative (6c), both when crystallized by itself and as a 1 : 1 acetone solvate, have a similar geometry and *syn*-arrangement of the two phenyl rings about the C(10)–N(2) amide bond. The other molecule of (6b) has an *anti*-arrangement about the C–N amide bond and is quite similar in conformation to those of the previously reported benzoylhydrazones (3a) and (3b). This group of molecules may be divided into two classes as evidenced by detailed analysis of the amide group geometry, the *syn*-class having very large pyramidal distortion at N (0.18—0.24 Å), and an intramolecular C=O • • • C=O interaction (2.67—2.84 Å), the *anti*-class being less overcrowded around the amide bond and showing less distortion at nitrogen. These features are reflected in ν(CO) values, being *ca.* 1 650 cm^{-1} for (3a) and (3b), which are relatively undistorted, and for the *syn*-hydrazone (6a) *ca.* 1 700 cm^{-1}. The crystal structure of (6b) shows a short (3.168 Å) Br • • • O intermolecular contact, which may be partly responsible for the presence of two rotamers in the crystal.

IN recent years there has been considerable interest in organic chemical reactions carried out in the crystalline state.[1,2] The thermal rearrangements converting azotriketones (1) into enol benzoates (2) and benzoylhydrazones (3), and also (2) into (3), have been studied in solution and in the solid state.[3,4] The investigation of a structurally-related family of compounds (4)—(6) was of interest because the enol benzoate (5), if formed, would necessarily have the *cis*-configuration of the

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[1] G. M. J. Schmidt, *Pure and Appl. Chem.*, 1971, **27**, 647; M. D. Cohen and B. S. Green, *Chem. in Brit.*, 1973, 490; J. M. Thomas, *Phil. Trans. Roy Soc.*, 1974, *A*, **277**, 251.

[2] I. C. Paul and D. Y. Curtin, *Accounts Chem. Res.*, 1973, **6**, 217; *Science*, 1975, **187**, 19; I. C. Paul and D. Y. Curtin, in 'Environmental Effects on Molecular Structure and Properties,' ed. B. Pullman, D. Reidel Publishing Co., Dordrecht, 1976, pp. 307—327.

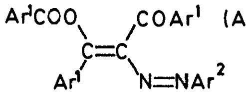
[3] (*a*) D. B. Pendergrass, jun., D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.*, 1972, **94**, 8722; (*b*) D. B. Pendergrass, jun., I. C. Paul, and D. Y. Curtin, *ibid.*, p. 8730.

[4] See C. S. Russell and D. Weisleder, *J. Org. Chem.*, 1967, **32**, 2626; C. S. Russell, K. Strothkamp, and D. Kasprisin, *ibid.*, 1969, **34**, 231.

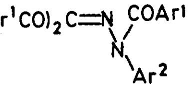
phenylazo- and benzoyloxy-groups about the carbon–carbon double-bond whereas the previous enol benzoates

$(Ar^1CO)_3CN{=}NAr^2$

(1)



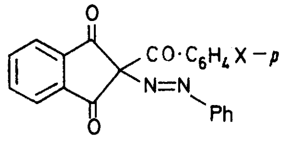
(2)



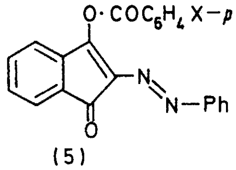
(3)

a; $Ar^1 = Ar^2 = Ph$
b; $Ar^1 = Ph$, $Ar^2 = 4\text{-}BrC_6H_4$.

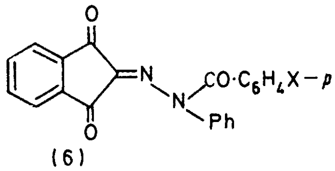
have been shown to be *trans*.[3,4] During the investigation, the synthesis of (4a) and (4b) was readily accomplished but their rearrangement was accompanied



(4)



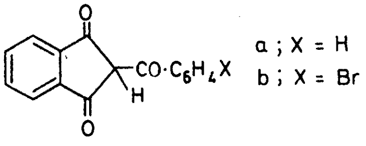
(5)



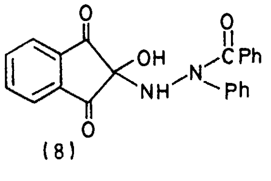
(6)

a; X = H c; $X = Bu^t$
b; X = Br d; $X = NO_2$

by cleavage to the triketone (7) and the rearrangement products presented unexpected spectral properties and chemical behaviour. No evidence was found for the accumulation of enol benzoates (5) as reaction products.



(7)



(8)

This paper presents the crystal structures of (6a) and (6b) determined in order to demonstrate that these are the compounds obtained in the solution rearrangement of (4a) and (4b). The significance of the conformations of the constituent molecules of (6a) and (6b) is discussed with respect to their spectral properties and to the possible acyl migration interconverting (5) and (6). Some comparisons of intramolecular structures of (6a) and (6b) with those of the t-butyl derivative (6c), determined in the crystal as a 1 : 1 acetone solvate,[5a] and of the related carbinol hydrazine (8),[6] will also be made. A few comparisons will be included with the structures of an unsolvated form of (6c) [5b] and of (6a) in a 1 : 1 complex with indane-1,2,3-trione 2-(*N*-phenylhydrazone).[5c]

EXPERIMENTAL

Spectra and other experimental details are available in ref. 7.

α-(p-*Bromobenzoyl*)-α-*phenylhydrazine*.—A modification of the procedure [8] for α-benzoyl-α-phenylhydrazine was employed. A slurry of the sulphate salt, obtained by hydrolysis of β-acetyl-α-(*p*-bromobenzoyl)-α-phenylhydrazine with sulphuric acid, was neutralized with an aqueous sodium carbonate solution. The resulting white solid was recrystallized from methanol (m.p. 134—135 °C); i.r. (Nujol) 1 630 cm^{-1} (Found: C, 53.7; H, 4.0; Br, 27.5; N, 9.9. Calc. for $C_{13}H_{11}N_2OBr$: C, 53.6; H, 3.8; Br, 27.4; N, 9.7%).

Indane-1,2,3-*trione* 2-(N-*Benzoyl*-N-*phenylhydrazone*) (6a).—(a) *From benzoylation of indane*-1,2,3-*trione* 2-(N-*phenylhydrazone*). A fourfold excess of benzoyl chloride was added to a solution of the phenylhydrazone (2.5 g) [9-11] in dry pyridine (50 ml), when the yellow reaction solution gradually became red. After 24 h at room temperature ether (200 ml) was added and the pyridine was extracted by successive washings with acidified water. The ether layer was separated, dried ($MgSO_4$), then evaporated quickly at room temperature to give a red oil which solidified when set aside to give a red solid (1.19 g; 84%), recrystallizable from acetone [m.p. 188—190 °C (decomp.)]; i.r. ($CHCl_3$), 1 700br and 1 738 cm^{-1}; u.v.-visible (MeCN), λ 372 (ε 10 600) and 474 nm (2 800); d.s.c. endotherm at 189 °C corresponds to melting, followed immediately by exothermic decomposition (Found: C, 74.4; H, 3.9; N, 8.0. Calc. for $C_{22}H_{14}N_2O_3$: C, 74.6; H, 4.0; N, 7.9%).

(b) *From ninhydrin and* α-*benzoyl*-α-*phenylhydrazine*. To a solution of ninhydrin (1.78 g, 0.01 mol) in glacial acetic acid (50 ml) was added a solution of α-benzoyl-α-phenylhydrazine (2.12 g, 0.1 mol) in methanol (20 ml). After 24 h at 25 °C, solvent was evaporated below room temperature, and the residue recrystallised from acetone as red tablets of (6a) (m.p. 189—190 °C); spectral and t.l.c. properties were identical with those of a sample of (6a) prepared by method (*a*).

Indane-1,2,3-*trione* 2-(N-p-*Bromobenzoyl*-N-*phenylhydrazone*) (6b).—The procedure employed was a modification of method (*a*) used to produce (6a). A solution of indanetrione phenylhydrazone (5 g) in dry pyridine (200 ml) was treated with *p*-bromobenzoyl chloride (17.6 g). After 4 h

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[5] (*a*) S. A. Puckett, I. C. Paul, and D. Y. Curtin, *J.C.S. Perkin II*, 1976, 1873; (*b*) R. A. Booker, I. C. Paul, and D. Y. Curtin, unpublished data; (*c*) J. A. McMillan, I. C. Paul, and D. Y. Curtin, unpublished data.

[6] S. A. Puckett, I. C. Paul, and D. Y. Curtin, *J. Amer. Chem. Soc.*, 1976, **98**, 787, 2371.

[7] S. A. Puckett, Ph.D. Thesis, University of Illinois, 1975. Available from University Microfilms, Ann Arbor, Michigan. The structure of (6b) has been refined extensively beyond the results presented herein. Much of the *X*-ray data in this reference is tabulated incorrectly.

[8] A. Michaelis and F. Schmidt, *Ber.*, 1887, **20**, 1713.

[9] W. Wislicenus and F. Reitzenstein, *Annalen.*, 1893, **277**, 362.

[10] A. Perjéssy and P. Hrnčiar, *Tetrahedron*, 1971, **27**, 6159.

[11] H. C. Yao, *J. Org. Chem.*, 1964, **29**, 2959.

at 25 °C, the red pyridine solution was poured into toluene (500 ml) and water (150 ml). The organic layer was washed with acidified water, separated, dried, and evaporated under reduced pressure below room temperature to give a yellow solid (8.7 g) essentially quantitatively. An analytical sample, prepared by slow evaporation of a saturated ether–iso-octane solution as clear yellow rods had m.p. 180—183 °C; i.r. ($CHCl_3$) 1 700br and 1 732 cm^{-1}; u.v.-visible (MeCN) $\lambda_{max.}$ 372 (ε 11 200) and 474 nm (3 170); d.s.c. endotherm at 191 °C followed by broad exotherm centred at 230 °C (Found: C, 61.1; H, 3.3; Br, 18.6; N, 6.6. Calc. for $C_{22}H_{13}N_2O_3Br$: C, 61.0; H, 3.0; Br, 18.4; N, 6.5%).

2-Benzoyl-2-phenylazoindane-1,3-dione (4a).—A solution of 2-benzoylindane-1,3-dione (7a) [12] (12.5 g, 0.05 mol) in ethyl acetate (200 ml) was treated with potassium carbonate (6.9 g, 0.1 mol). Upon refluxing for *ca.* 15 min on a steam bath, a brittle yellow solid was deposited as a layer on the sides of the flask. After heating under reflux for 0.5 h, the filtered yellow solid was air dried, and used without further purification in subsequent coupling reactions.

To a solution of this potassium salt (2.8 g) and sodium acetate (10.0 g) in water (100 ml) at 0 °C was added slowly a separate cold solution of benzenediazonium chloride which had been adjusted to pH 8 with 1M-sodium hydroxide solution immediately beforehand. Almost immediately a bright yellow precipitate formed, which after stirring for 0.5 h at 0°, was filtered and air dried. It was best recrystallized from ether–iso-octane or acetone–hexane as bright yellow needles, m.p. 125—130 °C (heating rate 10° min^{-1}), the m.p. varied with the rate of heating; i.r. ($CHCl_3$) 1 644, 1 706, and 1 757 cm^{-1}; u.v. (MeOH) $\lambda_{max.}$ 241 nm (ε 5.37 $\times$ 10^4); d.s.c. showed a slight endotherm at 127° followed immediately by a large exotherm (Found: C, 74.5; H, 4.1; N, 8.0. Calc. for $C_{22}H_{14}N_2O_3$: C, 74.6; H, 4.0; N, 7.9%).

*2-(*p*-Bromobenzoyl)-2-phenylazoindane-1,3-dione* (4b).—The triketone (7b) was prepared from dimethyl phthalate and *p*-bromoacetophenone according to the procedure used for (7a).[12] It was recrystallized once from acetone as light yellow needles, m.p. 175—177 °C. The i.r. spectrum of (7b) was nearly identical to that of (7a). The bromotriketone (7b) was then used without further purification.

An alternative procedure for preparing the potassium salt of (7b) was devised, owing to the limited solubility of (7b) in ethyl acetate. In a large Soxhlet extractor shell was placed the triketone (7b) (14.5 g). The Soxhlet extractor was then placed in a flask (1 l) which contained ethyl acetate (500 ml) and potassium carbonate (10.0 g). The mixture was then heated vigorously under reflux on a steam bath under dry nitrogen. As the triketone was extracted by the hot solvent and introduced into the reaction flask, a bright yellow precipitate quickly formed. After 3 h nearly all of (7b) had been extracted. The reaction mixture was cooled to 25 °C and the filtered solid air-dried; it was then used without further purification.

Owing to the insolubility of the potassium salt of 2-(*p*-bromobenzoyl)indane-1,3-dione in water, the coupling procedure was slightly modified. To a slurry of finely ground sodium acetate (10.0 g) in tetrahydrofuran was added a saturated solution of the potassium salt (3.67 g) of 2-(*p*-bromobenzoyl)indane-1,3-dione in tetrahydrofuran. After cooling the resulting mixture to 0 °C, a freshly prepared cold solution of benzenediazonium chloride at pH 8 was added dropwise, and ice also added. Upon complete addition of the diazonium salt the reaction mixture was stirred for 0.5 h at 0 °C, then diluted with ether (500 ml). The organic layer was separated and washed ($\times$ 3) with an equivalent volume of water. The ether solution was dried ($MgSO_4$) and evaporated below room temperature to give a yellow solid, which when recrystallized ($\times$ 2) from ether–iso-octane gave yellow needles, m.p. 120—125 °C (heating rate 10° min^{-1}); i.r. ($CHCl_3$) 1 679, 1 726, and 1 760 cm^{-1}; d.s.c. shows only a large exotherm at *ca.* 140—143 °C (Found: C, 60.8; H, 3.0; Br, 18.5; N, 6.5. Calc. for $C_{22}H_{13}BrN_2O_3$: C, 61.0; H, 3.0; Br, 18.4; N, 6.5%).

*2-Benzoyl-2-(*p*-nitrophenylazo)indane-1,3-dione* (4d).—A slurry of the potassium salt of 2-benzoylindane-1,3-dione (5.76 g, 0.02 mol) [12] and sodium acetate (15 g) in tetrahydrofuran (200 ml) was cooled to −78 °C, and *p*-nitrobenzenediazonium fluoroborate (4.74 g, 0.02 mol) then added in portions. Almost immediately the tetrahydrofuran layer began to turn bright yellow. Upon complete addition of the diazonium salt the reaction mixture was stirred for 45 min at −78°, then for 15 min at ambient temperatures. To the yellow layer was added diethyl ether (250 ml) and insoluble inorganic salts filtered off. The organic layer was washed with several small portions of water, and a bright yellow precipitate then formed which was filtered off. The ether layer was evaporated at $\leqslant$0 °C to give more yellow solid (total crude product 5.1 g, 64%). A portion was recrystallized from ether–iso-octane as yellow needles, m.p. 144—146 °C (Found: C, 66.2; H, 3.4; N, 10.6. Calc. for $C_{22}H_{13}N_3O_5$: C, 66.1; H, 3.3; N, 10.6%).

Recrystallization from acetone or benzene gave solvated crystals of unknown stoicheiometry. When removed from the mother liquor they rapidly lost the incorporated solvent, giving a microcrystalline material, m.p. 144—146 °C.

Thermal Rearrangement of 2-Benzoyl-2-phenylazoindane-1,3-dione (4a).—A solution of (4a) (0.055 6 g, 0.156 mmol) in toluene (0.5 ml) was heated at 100 °C under nitrogen. Aliquot portions of this solution were removed periodically and their i.r. spectra recorded. During heating, the toluene solution became red. The strong carbonyl absorptions at 1 667 and 1 719 cm^{-1}, which are characteristic of the spectrum of (4a), decreased in intensity, and after 2 h at 100 °C had decreased *ca.* 50%. Two new absorptions, 1 644 and 1 695 cm^{-1}, were observed, the former attributed to 2-benzoylindane-1,3-dione (7a), and the latter to the rearrangement product indanetrione 2-(*N*-benzoylphenylhydrazone) (6a). Analysis of the reaction after 2 h by t.l.c. showed large amounts of starting material and confirmed the presence of the benzoyl phenylhydrazone (6a) and the triketone (7a) in the reaction mixture. After 8 h at 100 °C, there were no carbonyl absorptions due to the azo-triketone in the i.r. spectrum. The ratio of the rearrangement product (6a) to the triketone (7a) after 8 h at 100 °C was estimated as 2 : 3.

A solution of 2-benzoyl-2-phenylazoindane-1,3-dione (0.23 g, 0.6 mmol) in toluene (10 ml) was heated under reflux for 2 h, when the solvent was evaporated under a stream of nitrogen. The residue was crystallized once from acetone–hexane as red crystals (0.085 g, 38%) of (6a): m.p. 182—188 °C, with i.r. and t.l.c. properties identical with those of an authentic sample of (6a). Also isolated from the reaction residue was a light yellow crystalline

[12] L. B. Kilgore, J. H. Ford, and W. C. Wolfe, *Ind. and Eng. Chem.*, 1942, **34** 494.

solid identified [t.l.c. and m.p. (106—108 °C)] as 2-benzoylindane-1,3-dione (7a).

Attempted Solid-state Rearrangement of 2-*Benzoyl*-2-*phenylazoindane*-1,3-*dione* (4a).—Single crystals of the azo-triketone were placed on a microscope slide and inserted into the Mettler FP 2 hot stage. The temperature range used was 80—100 °C. At constant temperatures of $\geqslant 100$ °C, crystals of (4a) became opaque in *ca.* 1 h, and began to change to an orange-red melt. Bubbles of gas were observed leaving the melt. After cooling the melt to room temperature, t.l.c. analysis indicated only minor amounts of the expected rearrangement product (6a). A large fraction of the melt consisted of the triketone (7a).

An investigation of the solid-state thermal behaviour of the azo-triketone at 80 °C produced similar results. After *ca.* 8 h at 80 °C, the crystals of (4a) had become quite opaque. The first signs of melting were observed after *ca.* 22 h at 80 °C. Trace amounts of the benzoylphenylhydrazone (6a) in the melt were detected by t.l.c.

Attempted Thermal Rearrangement of 2-(p-*Bromobenzoyl*)-2-*phenylazoindane*-1,3-*dione* (4b).—A toluene solution of analytically pure *p*-bromo-derivative (4b) was heated under reflux for 0.5 h under nitrogen, when the solution lightened to a pale yellow. Upon cooling to room temperature, solvent was evaporated under nitrogen, and a light yellow semi-solid residue was isolated. T.l.c. showed that no starting material remained, and that large quantities of 2-*p*-bromobenzoylindane-1,3-dione (7b) were present. Only traces of the possible rearrangement product, indanetrione 2-(*N*-*p*-bromobenzoyl-*N*-hydrazone) (6b) were identified by t.l.c. An unidentified, fast-moving, spot on t.l.c. was the only other product detected.

Attempted Solid-state Rearrangement of 2-(p-*Bromobenzoyl*)-2-*phenylazoindane*-1,3-*dione* (4b).—Two samples, large single crystals and fine needle-shaped crystals, of the azo-triketone (4b) were placed in screw cap vials and air flushed out with a gentle stream of argon. The vials were firmly sealed and heated under vacuum at 78.5 °C. All attempts were made to eliminate atmospheric water from the reaction chamber. After 2 days at 78.5 °C, the surfaces of the large crystals of (4b) became glossy golden yellow. The vial containing the smaller crystals contained small amounts of a light yellow sublimate on the top surface of the vial. As heating continued, both batches of crystals developed increasing amounts of the light yellow sublimate. During this time, the crystals of (4b) became dark brown. After 2.5 weeks, the crystals had become black and charred in appearance, so they were removed from the drying apparatus. Analysis of a portion of these crystals by t.l.c. showed two spots when eluted with benzene–chloroform (3 : 1). The first spot had identical t.l.c. properties to that of an authentic sample of 2-(*p*-bromobenzoyl)indane-1,3-dione (7b). The second spot moved fast on the t.l.c. plate and did not correspond to the expected rearrangement product (6b). The identity of this fraction of the reaction residue is unknown.

X-*Ray Structure Analysis of Indane*-1,2,3-*trione* 2-(N-*Benzoyl*-N-*phenylhydrazone*) (6a).—Red hexagonal-shaped crystals of (6a) prepared as described, were obtained from 1 : 1 acetone–hexane.

Crystal data. $C_{22}H_{14}N_2O_3$, $M = 354.4$. Monoclinic, $a = 6.774(2)$, $b = 28.950(11)$, $c = 9.018(3)$ Å, $\beta = 96.08(1)°$, $U = 1\,759$ Å^3, $D_m = 1.32$ g cm^{-3} (by flotation in aqueous $ZnCl_2$), $Z = 4$, $D_c = 1.34$ g cm^{-3}, $F(000) = 736$. Space group $P2_1/c$ from systematic absences: $h0l$ when $l = 2n + 1$, $0k0$ when $k = 2n + 1$. Cu-K_α radiation, $\lambda = 1.541\,78$ Å; μ(Cu-K_α) = 7.5 cm^{-1}. Cell dimensions were obtained by a least-squares fit to the settings of the angles for 12 high-angle reflections.

Intensity data were collected on a crystal with dimensions *ca.* 0.2 × 0.2 × 0.3 mm and mounted on a Picker FACS 1 diffractometer with the *a* axis of the crystal along the ϕ-axis of the diffractometer. General procedures for data collection were as described previously.[13] During data collection there was no evidence for crystal deterioration or loss of intensity. Of 3 262 reflections measured in the 2θ range 3—130°, 2 951 were considered observed at the 2σ significance level, based on counting statistics. No absorption corrections were applied.

TABLE 1

Final atomic co-ordinates (fractions of the unit cell) for the molecule (6a), with standard deviations in parentheses

	x	*y*	*z*
C(1)	0.510 5(3)	0.239 3(1)	0.172 8(2)
C(2)	0.474 7(3)	0.188 6(1)	0.185 3(2)
C(3)	0.633 6(3)	0.164 7(1)	0.112 1(2)
C(4)	0.750 3(3)	0.201 4(1)	0.048 5(2)
C(5)	0.911 9(3)	0.196 7(1)	−0.033 3(3)
C(6)	0.999 1(4)	0.235 9(1)	−0.080 8(3)
C(7)	0.925 4(4)	0.279 5(1)	−0.047 1(3)
C(8)	0.768 7(4)	0.284 4(1)	0.036 7(3)
C(9)	0.678 3(3)	0.244 5(1)	0.081 9(2)
C(10)	0.298 8(3)	0.098 8(1)	0.144 6(2)
C(11)	0.334 6(3)	0.048 6(1)	0.168 0(2)
C(12)	0.463 1(4)	0.031 8(1)	0.285 5(3)
C(13)	0.505 7(4)	−0.014 4(1)	0.295 3(3)
C(14)	0.416 1(4)	−0.044 5(1)	0.188 9(3)
C(15)	0.288 7(4)	−0.028 5(1)	0.073 4(3)
C(16)	0.248 2(3)	0.018 5(1)	0.061 1(3)
C(17)	0.214 8(3)	0.114 1(1)	0.402 2(2)
C(18)	0.284 4(4)	0.132 8(1)	0.538 4(2)
C(19)	0.191 9(4)	0.122 9(1)	0.664 4(3)
C(20)	0.035 1(4)	0.093 7(1)	0.655 2(3)
C(21)	−0.033 4(4)	0.073 9(1)	0.519 9(3)
C(22)	0.052 5(4)	0.085 0(1)	0.392 4(3)
O(1)	0.418 9(3)	0.270 1(1)	0.226 3(2)
O(2)	0.673 3(3)	0.123 7(1)	0.117 5(2)
O(3)	0.262 9(3)	0.115 3(1)	0.023 2(2)
N(1)	0.343 9(3)	0.173 7(1)	0.266 7(2)
N(2)	0.311 8(3)	0.126 8(1)	0.274 7(2)
H(5) *	0.970(4)	0.167(1)	−0.049(3)
H(6)	1.114(4)	0.234(1)	−0.146(3)
H(7)	0.991(4)	0.307(1)	−0.073(3)
H(8)	0.716(4)	0.314(1)	0.059(3)
H(12)	0.517(4)	0.053(1)	0.373(3)
H(13)	0.598(4)	−0.029(1)	0.372(3)
H(14)	0.448(4)	−0.076(1)	0.197(3)
H(15)	0.221(4)	−0.054(1)	−0.013(3)
H(16)	0.162(4)	0.035(1)	−0.020(3)
H(18)	0.402(4)	0.157(1)	0.546(2)
H(19)	0.242(4)	0.137(1)	0.765(3)
H(20)	−0.035(5)	0.095(1)	0.742(3)
H(21)	−0.135(4)	0.055(1)	0.509(3)
H(22)	0.013(5)	0.071(1)	0.302(3)

* Hydrogen atoms are given the number of the atom to which they are attached. A different numbering scheme for the hydrogen atoms was used in ref. 7.

The structure was solved by the symbolic addition procedure using FAME and the MAGIC–LINK–SYMPL series of programs.[14] Three cycles of full-matrix least-squares refinement, varying positional and isotropic thermal parameters for the 27 non-hydrogen atoms reduced R to 0.151 and R' to 0.198. All non-zero reflections were

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[13] R. S. Miller, I. C. Paul, and D. Y. Curtin, *J. Amer. Chem. Soc.*, 1974, **96**, 6334.

[14] D. B. K. Dewar, Ph.D. Thesis, University of Chicago, 1968.

weighted according to the method of Dieterich.[15] Introduction of anisotropic thermal parameters for the non-hydrogen atoms followed by further least-squares refinement reduced R to 0.090 and R' to 0.120. A difference map revealed the positions of the 14 hydrogen atoms. The addition of hydrogen atoms, with isotropic thermal parameters, required that the model be refined in two segments: (i) atoms C(10)—(22), N(2), O(3), and attached hydrogen atoms, and (ii) C(1)—(10), O(1)—(3), N(1), N(2), and attached hydrogen atoms. Further least-squares refinement on each fragment reduced R to 0.063 and R' to 0.073 for all non-zero reflections. In the final cycle of refinement, no parameter shifted by $>0.17\sigma$. The highest value of the electron density in a final difference map was 0.2 eÅ^{-3}. Final atomic co-ordinates are listed in Table 1, bond distances and angles in Table 2.

X-*Ray Structure Determination of Indane*-1,2,3-*trione* 2-(N-p-*Bromobenzoyl*-N-*phenylhydrazone*) (6b).—The hydrazone (6b) was obtained as yellow needles (m.p. 180—183 °C) by slow evaporation of a saturated ethereal solution.

Crystal data. $C_{22}H_{13}BrN_2O_3$, $M = 433.5$. Triclinic, $a = 15.369(14)$, $b = 13.917(17)$, $c = 9.195(8)$ Å; $\alpha = 99.50(7)°$, $\beta = 85.12(7)°$, $\gamma = 104.84(6)°$, $U = 1\,873$ Å^3; $D_m = 1.51$ g cm^{-3} (by flotation in aqueous KI), $Z = 4$; $D_c = 1.54$ g cm^{-3}, $F(000) = 872$. Space group $P1$ or $P\bar{1}$ (the latter confirmed by results of analysis). Cu-K_α radiation, $\lambda = 1.541\ 78$ Å; μ(Cu-K_α) = 35.3 cm^{-1}.

Cell parameters were determined by a least-squares fit to

TABLE 2

Bond lengths (Å) and angles (deg.) for (6a) *

C(1)–C(2)	1.494(3)	C(5)–C(6)–C(7)	120.3(3)
C(2)–C(3)	1.492(3)	C(6)–C(7)–C(8)	121.7(2)
C(3)–C(4)	1.476(3)	C(7)–C(8)–C(9)	117.8(2)
C(4)–C(5)	1.390(3)	C(8)–C(9)–C(4)	120.6(2)
C(5)–C(6)	1.371(4)	C(8)–C(9)–C(1)	129.5(2)
C(6)–C(7)	1.403(4)	C(9)–C(4)–C(5)	121.4(2)
C(7)–C(8)	1.375(4)	C(4)–C(9)–C(1)	109.9(2)
C(8)–C(9)	1.388(3)	C(10)–C(11)–C(12)	122.1(2)
C(4)–C(9)	1.385(3)	C(10)–C(11)–C(16)	117.8(2)
C(1)–C(9)	1.478(3)	C(11)–C(12)–C(13)	120.2(2)
C(10)–C(11)	1.483(3)	C(12)–C(13)–C(14)	119.7(2)
C(11)–C(12)	1.385(3)	C(13)–C(14)–C(15)	120.7(2)
C(12)–C(13)	1.370(4)	C(14)–C(15)–C(16)	119.8(2)
C(13)–C(14)	1.388(4)	C(15)–C(16)–C(11)	119.7(2)
C(14)–C(15)	1.361(4)	C(16)–C(11)–C(12)	119.8(2)
C(15)–C(16)	1.391(3)	C(17)–C(18)–C(19)	120.5(2)
C(11)–C(16)	1.383(3)	C(18)–C(19)–C(20)	120.0(2)
C(17)–C(18)	1.379(3)	C(19)–C(20)–C(21)	120.0(2)
C(18)–C(19)	1.385(3)	C(20)–C(21)–C(22)	120.5(2)
C(19)–C(20)	1.354(4)	C(21)–C(22)–C(17)	119.5(2)
C(20)–C(21)	1.382(4)	C(22)–C(17)–C(18)	119.4(2)
C(21)–C(22)	1.380(4)	C(9)–C(1)–O(1)	127.0(2)
C(17)–C(22)	1.379(3)	C(2)–C(1)–O(1)	126.6(2)
C(1)–O(1)	1.214(3)	C(1)–C(2)–N(1)	120.1(2)
C(3)–O(2)	1.216(3)	C(3)–C(2)–N(1)	132.1(2)
C(10)–O(3)	1.196(3)	C(2)–C(3)–O(2)	127.0(2)
C(2)–N(1)	1.284(3)	C(4)–C(3)–O(2)	126.3(2)
N(1)–N(2)	1.377(2)	C(2)–N(1)–N(2)	119.0(2)
C(10)–N(2)	1.423(3)	N(1)–N(2)–C(10)	121.1(2)
C(17)–N(2)	1.431(3)	N(1)–N(2)–C(17)	112.6(2)
C(1)–C(2)–C(3)	107.0(2)	C(10)–N(2)–C(17)	121.4(2)
C(2)–C(3)–C(4)	106.2(2)	N(2)–C(10)–O(3)	121.0(2)
C(2)–C(1)–C(9)	106.3(2)	N(2)–C(10)–C(11)	116.6(2)
C(3)–C(4)–C(5)	128.2(2)	N(2)–C(17)–C(18)	118.1(2)
C(3)–C(4)–C(9)	110.4(2)	N(2)–C(17)–C(22)	122.4(2)
C(4)–C(5)–C(6)	118.2(2)	O(3)–C(10)–C(11)	122.5(2)

* C–H lengths range from 0.88 to 1.13(3) Å, C–C–H angles from 112—127(2)°.

TABLE 3

Final atomic co-ordinates (fractions of the unit-cell edge) for the molecules of (6b), with standard deviations in parentheses

	x	y	z
Br(1)	0.289 3(1)	0.943 4(1)	0.570 8(1)
O(1)	0.768 8(3)	0.562 8(3)	−0.045 7(6)
O(2)	0.540 5(3)	0.592 4(3)	0.324 4(5)
O(3)	0.449 5(3)	0.593 2(4)	0.079 8(6)
N(1)	0.638 9(4)	0.678 1(4)	0.046 4(6)
N(2)	0.574 4(4)	0.728 3(4)	0.086 9(6)
C(1)	0.713 6(5)	0.546 8(5)	0.054 3(7)
C(2)	0.642 0(4)	0.601 7(4)	0.106 0(7)
C(3)	0.593 7(5)	0.559 0(5)	0.238 0(7)
C(4)	0.630 6(5)	0.473 2(5)	0.250 9(7)
C(5)	0.605 6(5)	0.408 0(5)	0.356 5(8)
C(6)	0.650 8(6)	0.332 3(6)	0.344 8(10)
C(7)	0.717 1(6)	0.323 2(6)	0.236 4(10)
C(8)	0.743 7(5)	0.390 1(5)	0.133 7(8)
C(9)	0.698 2(5)	0.464 1(5)	0.142 4(8)
C(10)	0.482 8(5)	0.678 3(6)	0.129 3(8)
C(11)	0.437 1(5)	0.743 4(5)	0.239 3(7)
C(12)	0.484 0(4)	0.817 8(5)	0.343 6(8)
C(13)	0.440 0(6)	0.874 3(5)	0.445 2(8)
C(14)	0.348 3(6)	0.859 4(5)	0.436 5(8)
C(15)	0.301 0(5)	0.787 3(6)	0.334 0(9)
C(16)	0.344 4(5)	0.728 0(5)	0.239 4(8)
C(17)	0.585 5(5)	0.815 2(5)	0.016 5(7)
C(18)	0.667 1(5)	0.882 6(6)	0.015 7(8)
C(19)	0.678 5(6)	0.963 3(6)	−0.060 1(10)
C(20)	0.608 9(7)	0.977 8(6)	−0.130 7(9)
C(21)	0.527 1(7)	0.910 6(7)	−0.127 5(9)
C(22)	0.5135 (5)	0.828 4(5)	−0.055 5(8)
H(5) [a]	0.561(3)	0.425(4)	0.432(6)
H(6)	0.632(5)	0.289(5)	0.436(8)
H(7)	0.743(4)	0.268(4)	0.235(6)
H(8)	0.790(4)	0.381(4)	0.064(6)
H(12)	0.546(3)	0.826(3)	0.355(5)
H(13)	0.473(4)	0.912(4)	0.530(6)
H(15)	0.242(4)	0.776(4)	0.331(6)
H(16)	0.314(4)	0.677(4)	0.177(6)
H(18)	0.714(4)	0.869(4)	0.049(6)
H(19)	0.724(3)	1.007(4)	−0.050(5)
H(20)	0.615(4)	1.034(5)	−0.182(7)
H(21)	0.470(3)	0.923(4)	−0.162(5)
H(22)	0.462(3)	0.777(3)	−0.062(5)
Br(1′) [b]	0.891 5(1)	0.984 5(1)	−0.358 3(1)
O(1′)	0.873 5(3)	0.572 6(3)	0.341 2(6)
O(2′)	0.781 5(3)	0.863 4(3)	0.301 3(5)
O(3′)	1.134 0(4)	0.774 4(4)	0.035 4(6)
N(1′)	0.927 9(4)	0.776 9(4)	0.206 9(6)
N(2′)	1.002 2(4)	0.741 5(4)	0.171 6(6)
C(1′)	0.844 6(4)	0.646 3(5)	0.374 5(7)
C(2′)	0.867 5(4)	0.740 1(5)	0.302 5(7)
C(3′)	0.793 6(4)	0.791 4(5)	0.348 8(7)
C(4′)	0.741 3(4)	0.742 5(5)	0.470 6(7)
C(5′)	0.670 9(5)	0.766 0(6)	0.558 4(9)
C(6′)	0.630 2(5)	0.704 2(8)	0.661 1(9)
C(7′)	0.659 9(6)	0.620 7(7)	0.674 1(8)
C(8′)	0.730 5(5)	0.595 4(6)	0.585 5(8)
C(9′)	0.770 6(4)	0.658 4(5)	0.483 4(7)
C(10′)	1.056 5(5)	0.779 3(5)	0.048 0(8)
C(11′)	1.013 5(5)	0.825 0(5)	−0.051 6(7)
C(12′)	0.925 7(5)	0.786 4(5)	−0.094 4(7)
C(13′)	0.890 3(5)	0.831 3(5)	−0.190 4(8)
C(14′)	0.943 8(5)	0.916 6(5)	−0.239 5(7)
C(15′)	1.031 3(5)	0.955 0(5)	−0.203 9(8)
C(16′)	1.066 1(5)	0.907 7(5)	−0.109 9(9)
C(17′)	1.041 0(4)	0.694 6(5)	0.269 7(9)
C(18′)	1.049 1(5)	0.739 4(5)	0.415 9(9)
C(19′)	1.082 2(5)	0.690 3(7)	0.512 8(9)
C(20′)	1.104 1(5)	0.601 8(7)	0.466 1(13)
C(21′)	1.097 9(5)	0.560 7(6)	0.317 4(12)
C(22′)	1.064 2(5)	0.606 3(5)	0.219 8(9)
H(5′)	0.651(3)	0.834(4)	0.550(6)
H(6′)	0.581(4)	0.721(4)	0.711(6)
H(7′)	0.633(4)	0.583(4)	0.743(6)
H(8′)	0.752(3)	0.533(3)	0.582(5)
H(12′)	0.891(3)	0.723(4)	−0.072(6)

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[15] D. A. Dieterich, Ph.D. Thesis, University of Illinois, 1973.

TABLE 3 (*Continued*)

	x	y	z
H(13′)	0.827(4)	0.815(4)	−0.200(6)
H(15′)	1.070(4)	1.020(4)	−0.234(6)
H(16′)	1.129(4)	0.933(4)	−0.091(6)
H(18′)	1.033(3)	0.809(4)	0.443(6)
H(19′)	1.084(3)	0.728(4)	0.603(6)
H(20′)	1.125(4)	0.564(5)	0.543(7)
H(21′)	1.112(4)	0.501(5)	0.286(7)
H(22′)	1.057(3)	0.572(4)	0.104(6)

[a] See footnote to Table 1. [b] This atom was designated Br(2) in ref. 7. *syn*-form unprimed, *anti*-form primed.

the angular settings for eight high-order reflections. Intensity data were collected on a crystal with dimensions *ca.* 0.15 × 0.15 × 0.3 mm along the *a*, *b*, and *c* axes, respectively.[13] The crystal was mounted on a Picker FACS 1 diffractometer with the [001] direction of the crystal along the ϕ axis of the diffractometer. Procedures were as described previously. There was no evidence for crystal decay during data collection. Of a total of 7 027 reflections measured, 4 425 were considered observed at the 2σ level.

The structure was solved by Patterson and heavy-atom methods based on bromine. Least-squares refinement of positional and isotropic thermal parameters for all non-hydrogen atoms in the two crystallographically-independent molecules reduced R to 0.177 and R' to 0.189. A difference map at this time revealed only a portion of the hydrogen atoms in the two molecules. The remaining hydrogen atom positions were calculated assuming standard criteria for dimensions. Least-squares refinement of positional and anisotropic thermal parameters for the non-hydrogen atoms and positional and isotropic thermal parameters for the hydrogen atoms required that the structure be refined in three parts. The atoms in the crystal asymmetric unit were divided into three parts: the non-hydrogen atoms of one molecule, the non-hydrogen atoms of the second molecule, and the hydrogen atoms of both molecules. These parts were refined in turn to convergence and R and R' were reduced to 0.081 and 0.080, respectively. The largest peaks in a final difference electron density map were of height 0.6—0.8 eÅ^{-3} and were all within 1 Å of a bromine atom. Final atomic co-ordinates are listed in Table 3, bond lengths and angles in Table 4. The atomic scattering factors for the non-hydrogen atoms in both *X*-ray analyses were taken from ref. 16, and for hydrogen atoms from ref. 17. Observed and calculated structure factors and the values for the thermal parameters from both *X*-ray analyses are

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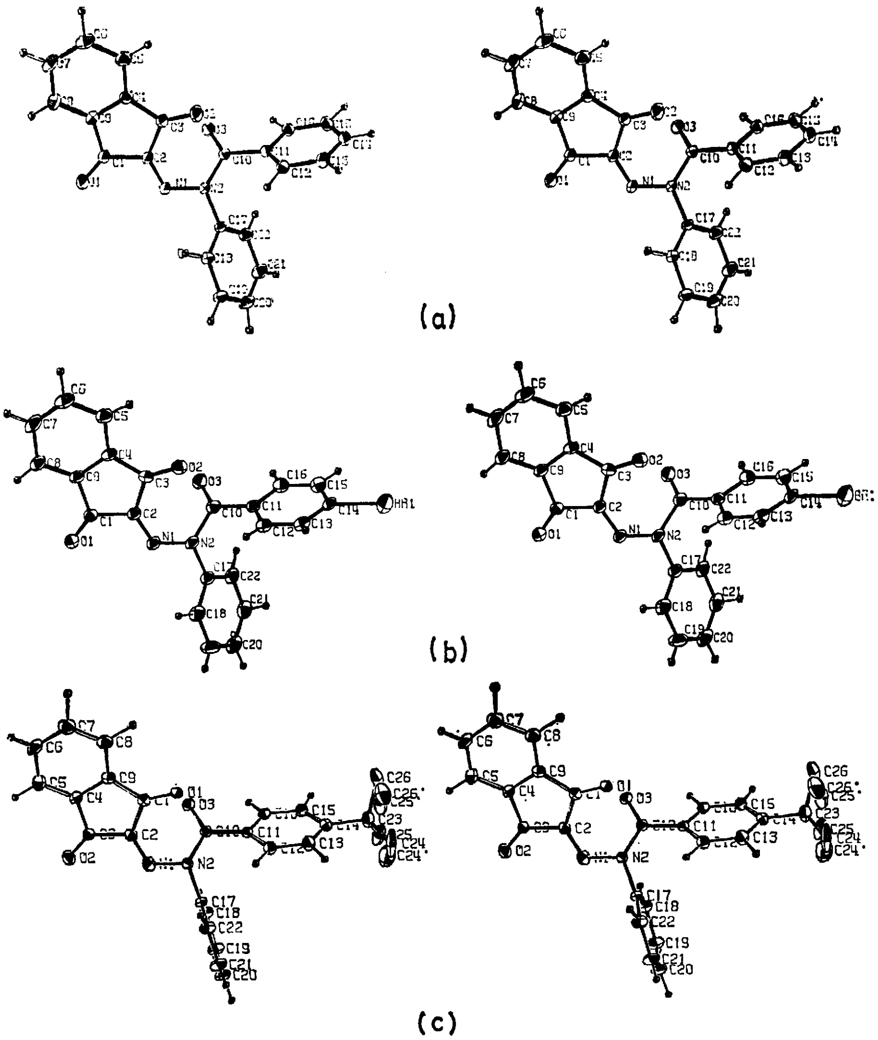
[16] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[17] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.



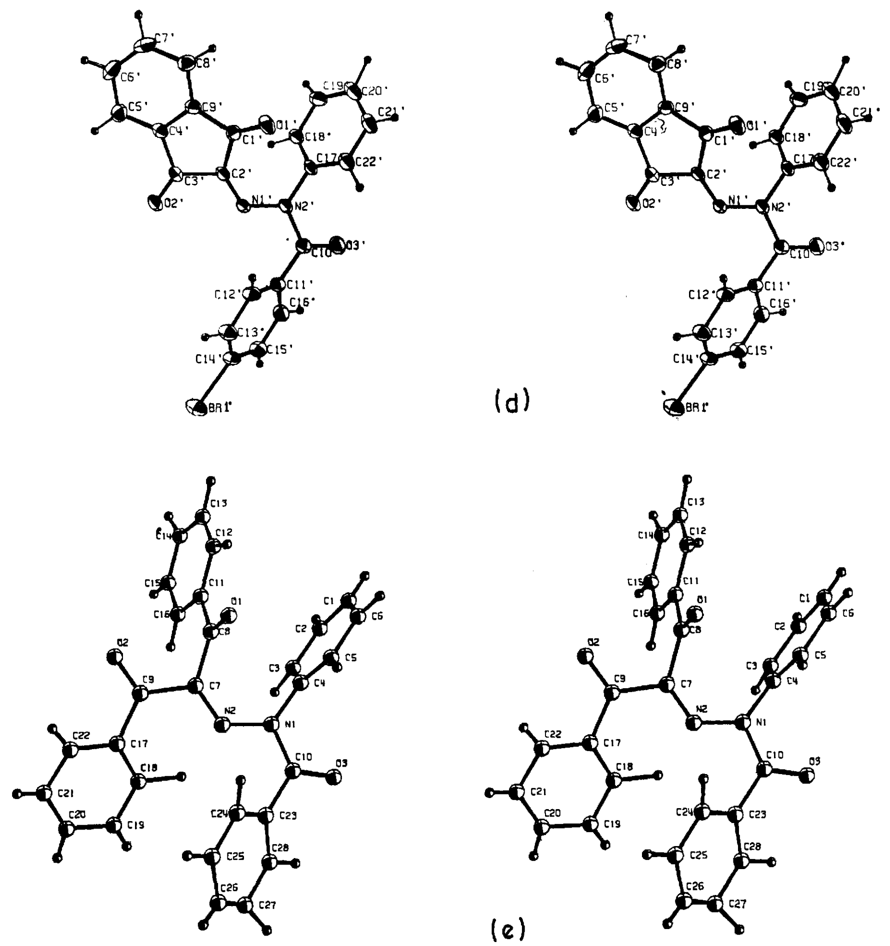


FIGURE 1 Stereoscopic views of five molecules oriented with the N–N bond horizontally in the plane of the page: (a) (6a), (b) *syn*-(6b), (c) (6c) (ref. 5; the t-butyl group is disordered), (d) *anti*-(6b), and (e) (3a) (ref. 3*b*). Atom numbering used in this molecule is as given in ref. 3*b* and differs somewhat from that used for molecules (6a), (6b), and (6c). Atoms are numbered such that O(2) approaches O(3) in (6a) and *syn*-(6b), whereas O(1) approaches O(3) in (6c) and *anti*-(6b).

listed in Supplementary Publications No. SUP 21658 (63 pp., 1 microfiche).*

RESULTS AND DISCUSSION

Stereoscopic drawings of the molecule of (6a), the two molecules of (6b), the molecule (6c),[5a] and the molecule of (3a),[3b] similarly oriented, are shown in Figure 1. Bond lengths and angles for (6a) and (6b) (Tables 2 and 4) are in agreement with those found in similar structures [18,19] and, in general, do not require discussion.

Although the studies were carried out on samples synthesized independently, these were identical to the products of the thermal rearrangements. The *X*-ray analyses therefore clearly establish that the red and yellow products of the thermal rearrangements of (4a) and (4b) are the benzoylphenylhydrazones (6a) and (6b). An unusual feature of the structure of (6b) in the crystal is the existence of two rotamers about the N(2)–C(10) bond. The molecule whose atoms are unprimed in Table 3, and which is shown in Figure 1(b), has the phenyl groups on the same side of the N(2)–C(10) bond and will be designated the *syn*-, and the primed molecule [Figure 1(d)] the *anti*-isomer. A comparison of the conformations of benzoylphenylhydrazones (6a) and (6b) with related compounds [(3a),[3b] (3b),[3b] and two forms of (6c) [5a,b] and (6a) in a complex with indane-1,2,3-trione 2-(*N*-phenylhydrazone) [5c]] shows that in each case the molecular conformation in the crystal falls into one of two types: a *syn*-conformation similar to that of (6a) [this group includes *syn*-(6b) and (6c) in Figure 1(a)—(c) and the other forms of (6a) [5c] and (6c) [5b]], or an *anti*-conformation similar to *anti*-(6b) [this group includes (3a) and (3b); *anti*-(6b) and (3a) are shown in Figure 1(d) and (e)]. The conformational uniformity in each of these series is confirmed further in the analysis of the torsion angles of atoms attached to the amide C–N bonds (see later). This is the more remarkable because these conformations occur in

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* For details, see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1976, Index issue.

[18] W. Bolton, *Acta Cryst.*, 1965, **18**, 5.

[19] F. Bechtel, G. Bravic, J. Gaultier, and C. Hauw, *Cryst. Struct. Comm.*, 1972, **1**, 159; *Acta Cryst.*, 1974, **B30**, 1499. See also G. Bravic, J. Gaultier, and C. Hauw, *Cryst. Struct. Comm.*, 1974, **3**, 215; 1974, **3**, 219 for other 2-phenylindane-1,3-dione structures.

crystals having a variety of packing arrangements, crystal symmetries, and space groups.

TABLE 4

Bond lengths (Å) and bond angles (°) for the molecules of (6b), with standard deviations in parentheses *

	syn	*anti*		*syn*	*anti*
N(1)–N(2)	1.348(8)	1.351(8)	N(1)–C(2)–C(1)	119.4(6)	135.5(6)
O(1)–C(1)	1.205(9)	1.204(8)	N(1)–C(2)–C(3)	132.7(6)	117.9(6)
N(1)–C(2)	1.287(8)	1.290(9)	C(1)–C(2)–C(3)	107.4(5)	106.3(5)
C(1)–C(2)	1.498(10)	1.509(9)	O(2)–C(3)–C(2)	127.6(6)	126.7(6)
O(2)–C(3)	1.215(9)	1.218(8)	O(2)–C(3)–C(4)	126.5(6)	126.5(6)
C(2)–C(3)	1.495(9)	1.487(10)	C(2)–C(3)–C(4)	105.6(6)	106.7(5)
C(3)–C(4)	1.471(10)	1.477(9)	C(3)–C(4)–C(5)	127.2(6)	130.0(7)
C(4)–C(5)	1.401(10)	1.370(11)	C(3)–C(4)–C(9)	110.8(6)	109.1(6)
C(5)–C(6)	1.389(12)	1.384(13)	C(5)–C(4)–C(9)	121.9(6)	120.7(7)
C(6)–C(7)	1.379(13)	1.378(14)	C(4)–C(5)–C(6)	116.2(7)	118.5(8)
C(7)–C(8)	1.398(11)	1.385(12)	C(5)–C(6)–C(7)	121.5(8)	120.6(8)
C(1)–C(9)	1.474(9)	1.473(10)	C(6)–C(7)–C(8)	122.2(8)	121.6(8)
C(4)–C(9)	1.393(10)	1.382(10)	C(7)–C(8)–C(9)	116.7(7)	117.0(7)
C(8)–C(9)	1.373(10)	1.388(10)	C(1)–C(9)–C(4)	109.6(6)	111.1(6)
N(2)–C(10)	1.454(9)	1.441(9)	C(1)–C(9)–C(8)	128.9(6)	127.3(6)
O(3)–C(10)	1.193(9)	1.205(10)	C(4)–C(9)–C(8)	121.4(6)	121.5(7)
C(10)–C(11)	1.497(10)	1.480(10)	N(2)–C(10)–O(3)	121.7(7)	118.2(7)
C(11)–C(12)	1.385(10)	1.383(11)	N(2)–C(10)–C(11)	113.5(6)	117.2(6)
C(12)–C(13)	1.367(11)	1.380(10)	O(3)–C(10)–C(11)	124.8(7)	124.6(7)
Br(1)–C(14)	1.895(8)	1.900(7)	C(10)–C(11)–C(12)	122.3(6)	123.4(6)
C(13)–C(14)	1.378(13)	1.379(10)	C(10)–C(11)–C(16)	119.2(6)	117.6(6)
C(14)–C(15)	1.362(11)	1.360(11)	C(12)–C(11)–C(16)	118.4(7)	119.0(7)
C(11)–C(16)	1.385(11)	1.385(10)	C(11)–C(12)–C(13)	121.0(7)	120.5(7)
C(15)–C(16)	1.352(11)	1.383(11)	C(12)–C(13)–C(14)	118.5(7)	118.4(7)
N(2)–C(17)	1.430(8)	1.442(9)	Br(1)–C(14)–C(13)	118.0(6)	118.2(5)
C(17)–C(18)	1.360(11)	1.387(11)	Br(1)–C(14)–C(15)	120.5(6)	119.0(5)
C(18)–C(19)	1.384(11)	1.406(11)	C(13)–C(14)–C(15)	121.4(7)	122.9(7)
C(19)–C(20)	1.370(14)	1.352(13)	C(14)–C(15)–C(16)	119.6(8)	117.8(7)
C(20)–C(21)	1.364(14)	1.393(16)	C(11)–C(16)–C(15)	121.0(7)	121.3(7)
C(17)–C(22)	1.402(11)	1.364(10)	N(2)–C(17)–C(18)	119.4(6)	117.9(6)
C(21)–C(22)	1.377(12)	1.382(12)	N(2)–C(17)–C(22)	119.9(6)	120.2(6)
N(2)–N(1)–C(2)	121.5(5)	121.3(6)	C(18)–C(17)–C(22)	120.6(7)	121.9(7)
N(1)–N(2)–C(10)	122.4(5)	114.8(5)	C(17)–C(18)–C(19)	119.0(7)	117.6(7)
N(1)–N(2)–C(17)	113.6(5)	123.9(5)	C(18)–C(19)–C(20)	121.4(8)	121.4(8)
C(10)–N(2)–C(17)	116.8(5)	118.9(6)	C(19)–C(20)–C(21)	119.2(9)	119.4(9)
O(1)–C(1)–C(2)	126.9(6)	127.9(6)	C(20)–C(21)–C(22)	121.1(9)	120.5(9)
C(2)–C(1)–C(9)	106.0(6)	105.2(6)	C(17)–C(22)–C(21)	118.7(7)	119.1(7)
O(1)–C(1)–C(9)	126.9(6)	126.5(6)			

* C–H lengths range from 0.82—1.13(7) Å, C–C–H angles from 116—126(4)°.

TABLE 5

Some details of the geometry of the C(:O)–N< group (distances Å, angles °)

	Carbinol Hydrazine	*anti*-Hydrazones				*syn*-Hydrazones			
	(8)	(3a)	(3b)	*anti*-(6b)	(6a)	*syn*-(6b)	(6c) [a]	(6c) [b]	(6a) [c]
Amide N–C [d]	1.370(3)	1.36(2)	1.41(1)	1.441(9)	1.423(3)	1.454(9)	1.409(5)	1.417(4)	1.412(5)
Amide C=O [e]	1.235(4)	1.23(1)	1.20(1)	1.205(10)	1.196(2)	1.193(9)	1.211(5)	1.207(4)	1.198(5)
Devn. N from plane [f]	0.04	0.10	0.13	0.13	0.18	0.22	0.24	0.22	0.22
Angle amide Ph to amide C(:O)N [g]	42	39	37	38	30	31	36	37	40
Angle N–Ph to amide C(:O)N group [h]	54	87	87	66	61	74	80	73	76

[a] The molecule of (6c) determined as a 1 : 1 acetone solvate. [b] The molecule of (6c) determined in a solvent-free crystal. [c] The molecule of (6a) determined in a 1 : 1 complex with indane-1,2,3-trione 2-(*N*-phenylhydrazone). [d] Numbered N(2)–C(10) for compounds (6a—c) and (8); numbered N(1)–C(10) for (3a) and (3b). [e] Numbered C(10)–O(3) for all compounds. [f] Deviation of N from plane of three bonded neighbours. [g] C(11)–C(16) to N(2)–C(10)–O(3) for (6a—c) and (8); C(23)–C(28) to N(1)–C(10)–O(3) for (3a) and (3b). [h] C(17)–C(22) to N(2)–C(10)–O(3) for (6a—c) and (8); C(1)–C(6) to N(1)–C(10)–O(3) for (3a) and (3b).

Geometry and Bonding at the Amide Nitrogen.—The separation of the benzoylhydrazones into *syn*- and *anti*-conformational classes is shown dramatically by consideration of the geometry of the amide bond and its surroundings. Views of torsion angles along the amide bond for (6a, both forms), (6b, both molecules), (6c, both forms), (3a), and (3b), and for (8) are shown in Figure 2, while some of the bond lengths and other geometric properties are compared in Table 5. Formally, the C(10)–N(2) bonds in (6a—c) would be considered as amide bonds. However, the C–N lengths are greater (Table 5) than those found in the acyclic hydrazones (3a) and (3b) [3b] or the carbinol hydrazine (8),[6] and much greater than the typical length for a peptide bond (1.325 Å).[20] These lengths in (6a—c) suggest less double-bond character in the C–N bond and

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[20] R. E. Marsh and J. Donohue, *Adv. Protein Chem.*, 1967, **22**, 235.

less delocalisation over the N–C–O group than is usual for amides. A distinction between the *syn*- and *anti*-classes can be made on the basis of the extent of non-planarity at the 'amide' nitrogen atom. Ideally, the six atoms comprising an amide group would be planar, due to partial double-bond character in the C–N bond. However, when bulky substituents are present, departures from planarity are quite common.[3b,21] One type of relief from overcrowding would involve twist around the C–N bond, while retaining planar configurations at nitrogen and at the carbonyl carbon. This type of effect is observed in (8)[6] [Figure 2(l)].

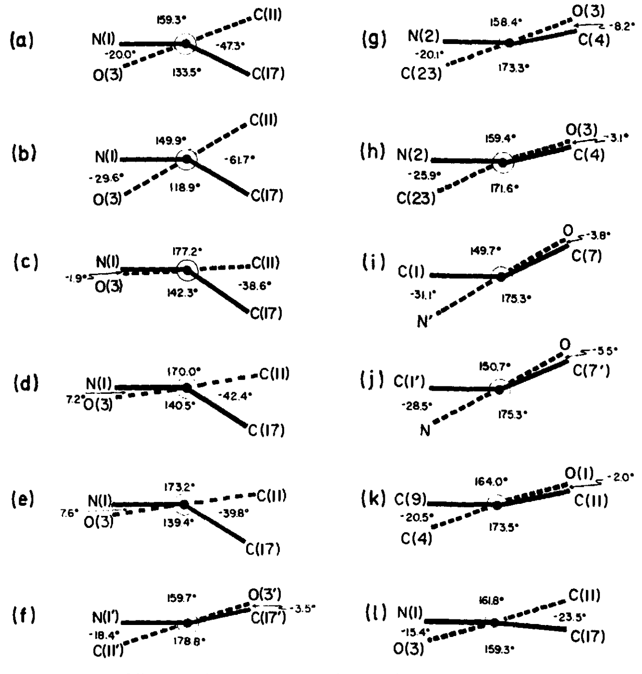
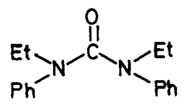
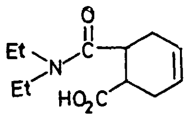


FIGURE 2 Views along the N–C (amide) bond in a series of molecules showing values of the torsion angles: (a) (6a), (b) *syn*-(6b), (c) (6c) as the 1 : 1 acetone solvate (ref. 5a), (d) (6c) in solvent-free crystal (ref. 5b), (e) (6a) in the 1 : 1 complex with indane-1,2,3-trione 2-(*N*-phenylhydrazone) (ref. 5c), (f) the *anti*-(6b) molecule (present work), (g) (3a) (ref. 3b), (h) (3b) (ref. 3b), (i) (9) looking along the N–C(C:) bond (ref. 22), (j) (9) looking along the N′–C(:O) bond (ref. 22), (k) (10) (ref. 23; the opposite enantiomorph from that defined in Table II of ref. 23 is presented here), and (l) (8) (ref. 6). Atom numbers are as given in the original papers

However, in most of these structures some relief from overcrowding is accomplished by a distortion of the geometry at nitrogen towards a pyramidal structure. These deviations from planarity at nitrogen can be seen in Figure 2. The pyramidal distortion of nitrogen from the plane defined by its three bonded neighbours shows a clear trend from the *syn*- (0.18—0.24 Å) to the *anti*-class (0.10—0.13 Å), down to the carbinol hydrazine (0.04 Å). Pyramidal distortions have been noted previously, in *e.g.* *NN*′-diethyl-*NN*′-diphenylurea (9)



(9)



(10)

(0.17 and 0.19 Å),[22] and 6-diethylcarbamoylcyclohex-3-enecarboxylic acid (10) (0.10 Å),[23] but not to the extent found in these *syn*-benzoylhydrazones. Torsion angles around the C–N bonds in (9) and (10) are also shown in Figure 2. In all the molecules shown there, except (6a) and *syn*-(6b), the carbonyl oxygen atom is almost eclipsed by the atom *syn* to it. The *anti*-(6b) molecule gains some stability by having the bulky phenyl groups disposed on opposite sides of the C(10)–N(2) bond, as was also the case for (3a) and (3b). In general, *N*-substituted amides crystallize in conformations with the bulkiest groups mutually *trans* or *anti* about the partial double-bond.[3b] It is possible that the loss of stability in the *syn*-class is offset, at least partially, by gains due to the intramolecular C=O · · · C=O interaction (see later). The overcrowding around the amide bonds is also alleviated by rotations of the phenyl rings out of the plane of the amide group (Table 5). In summary, there is a generally consistent picture in that the molecules with the *syn*-arrangement of bulky groups have the greatest pyramidal distortions at nitrogen.

Intramolecular C=O · · · C=O *Interactions*.—Inspection of Figure 1(a—c) shows the very close similarity in conformation between (6a), the *syn*-rotamer of (6b) and (6c) as the 1 : 1 acetone solvate.[5a] Common features of the geometry of (6a), *syn*-(6b), and (6c) are short intramolecular O(2) · · · C(10) [2.673(3), 2.638(9), and 2.835(7) Å] and O(2) · · · O(3) [2.830(3), 2.751(7), and 2.755(5) Å] distances. This type of contact has been recognised previously in the tribenzoyl(phenylazo)-methanes (1)—(3), where it was postulated that it might play a role in determining the products of the solid-state rearrangements.[3,24] In two tribenzoyl-(phenylazo)methanes with different packing arrangements,[3a] a nearly identical molecular conformation was found with the carbonyl oxygen atom of one benzoyl group pointing towards the carbon atom of the second benzoyl group, while the oxygen of the second group is directed towards the carbon of the third benzoyl group in the two molecules; these C · · · O distances ranged from 2.67 to 2.76 Å. A number of other cases,[25-27] where intramolecular C(CO) · · · O(CO) interactions play a role in determining conformation

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[21] F. K. Winkler and J. D. Dunitz, *J. Mol. Biol.*, 1971, **59**, 169.

[22] P. Ganis, G. Avitabile, E. Benedetti, C. Pedone, and M. Goodman, *Proc. Nat. Acad. Sci. U.S.A.*, 1970, **67**, 426. The *z*-co-ordinate of N(1) in this paper should be 0.351 7 instead of 0.331 7 (M. Goodman and G. Avitabile, personal communication, 1971).

[23] C. Pedone, E. Benedetti, A. Immirzi, and G. Allegra, *J. Amer. Chem. Soc.*, 1970, **92**, 3549.

[24] R. T. Puckett, C. E. Pfluger, and D. Y. Curtin, *J. Amer. Chem. Soc.*, 1966, **88**, 4637.

[25] A. H. Lowrey, C. George, P. D'Antonio, and J. Karle, *J. Amer. Chem. Soc.*, 1971, **93**, 6399.

[26] D. Rabinovich, G. M. J. Schmidt, and Z. Shaked, *J. Chem. Soc.* (*B*), 1970, 17.

[27] L. P. Kuhn, R. E. Lutz, and C. R. Bauer, *J. Amer. Chem. Soc.*, 1950, **72**, 5058.

have been noted.[3] The importance of CO · · · CO intermolecular interactions in determining packing effects has also been described.[28-30]

Recently, Dunitz and co-workers[31] have drawn a parallel between short O · · · C=O contacts and nucleophilic addition reaction pathways. They found, from a survey of both inter- and intra-molecular O · · · C=O contacts <3 Å, that the electron-deficient carbon atom is displaced from the plane defined by its three bonded neighbours towards the nucleophilic oxygen atom (Figure 3) by distances (Δ) ranging up to 0.10 Å. Dunitz and colleagues found that the displacement (Δ) generally increased as the O · · · C distance (d_2) decreased. However, the results found for (6a), *syn*-(6b), and the acetone solvate of (6c), where the interacting atoms, O(2) and C(10), are separated by five bonds, are somewhat anomalous. While the O · · · C distances (d_2) are quite short [2.673(3), 2.638(9), and 2.835(7) Å], the deviations from the plane (Δ) are very small (<0.006 Å), and tend to be in the direction opposite from the interacting O atom. There could be several explanations as to why the data from these structures fail to follow the correlations of Dunitz and colleagues. These authors did not list any examples of molecules with short (*i.e.* <2.9 Å) O · · · C=O contacts, where the angle α (Figure 3) was less than 87°; in (6a), *syn*-(6b), and the acetone solvate of (6c), the values of α are 85, 83, and 74°. Dunitz and colleagues also noted that most of the short O · · · C distances occurred when both the electrophile and the nucleophile were carbonyl groups, and the C=O(nucleophile) · · · C(electrophile) angle was in the range 150—180°, whereas these angles are 93.4, 94.6, and 90.6° in (6a), *syn*-(6b), and the acetone solvate of (6c). Thus the approach of the nucleophilic oxygen atom may not be along the correct pathway for interaction. Finally, the molecules (6a), *syn*-(6b), and (6c) appear to be the first examples in which the electrophilic centre is, at least formally, an amide group, although there is both geometric and spectroscopic evidence (see later) for significant lack of amide character in the N(2)–C(10) bonds.[32]

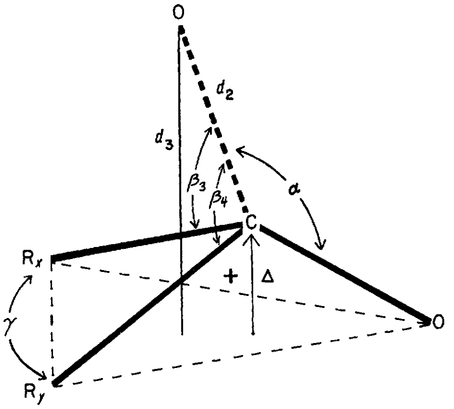

FIGURE 3 The relative disposition of atoms involved in O · · · C carbonyl contacts following the conventions of ref. 31. Bond angles R_x–C–O and R_y–C–O are denoted by β_1 and β_2

Spectroscopic Properties of the Benzoylhydrazones (3) *and* (6).—The division of these compounds into two quite different conformational classes would suggest that differences in the i.r. spectra might be interpreted in terms of the conformations observed in the solid state. As a starting point, the ' non-cyclic ' triketone benzoylhydrazones (3a) and (3b) were found to show the amide C=O stretching frequency as an absorption at *ca.* 1 650 cm^{-1}, incompletely resolved from the keto-carbonyl absorption at 1 680 cm^{-1}. Such an ' amide ' frequency is reasonable for the observed *anti*-conformation with a relatively small distortion from the planar amide group with the N(1)–N(2) and C(10)–O(3) bonds nearly *trans*. The *syn*-conformation, with a more pyramidal amide nitrogen and with nearly eclipsed N(1) and O(3), would be expected to have a carbonyl stretching vibration at higher frequencies. Such shifts to higher frequency are well-known for ketones such as dibenzoylbromomethane with an α-substituent having a significant dipole nearly *cis* and coplanar to the carbonyl group.[33] The carbonyl-stretching region of a number of indane-1,3-diones with a double bond at the 2-position has been analysed[10] and found to consist of two absorptions, one, the asymmetrical stretch, at *ca.* 1 660—1 688 cm^{-1} and a higher frequency absorption, the symmetrical stretch, in the region 1 707—1 728 cm^{-1}.

As expected, the *syn*-hydrazone (6a), with its carbonyl oxygen atom nearly eclipsed with the adjacent N–N bond, in chloroform solution or as a KBr disc, shows two indanetrione bands at 1 738 and 1 700 cm^{-1} (separation 38 cm^{-1} in agreement with the earlier work[10]), but no absorption maximum in the region near 1 650 where the *anti*-hydrazones (3a) and (3b) absorbed. Instead, the intensity of the 1 700 cm^{-1} band is a strong indication that in this isomer the ' amide ' carbonyl absorption has been shifted to higher frequency at *ca.* 1 700 cm^{-1}. The bromo-derivative (6b) shows a similar spectrum in solution (1 732 and 1 700 strong cm^{-1}). In the solid spectrum (KBr) there is a suggestion of an additional maximum at *ca.* 1 640 cm^{-1} to be expected of the second (*anti*) conformer found in the crystal structure. In view of the incomplete resolution of the absorptions, it can be said only that the spectra are consistent with the *X*-ray results.

Whereas the benzoylphenylhydrazones (6a—d) in

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[28] C. A. Maier, J. A. Kapecki, and I. C. Paul, *J. Org. Chem.*, 1971, **36**, 1299.

[29] B. Krebs and D. F. Koenig, *Acta Cryst.*, 1969, **B25**, 1022.

[30] W. Bolton, *Acta Cryst.*, 1964, **17**, 147.

[31] H. B. Bürgi, J. D. Dunitz, and E. Shefter, *Acta Cryst.*, 1974, **B30**, 1517.

[32] In this context, it may be noted that in the crystal structure of (1a)[3a] there are two short C=O · · · C=O distances (2.757 and 2.668 Å) where the interacting atoms are separated by two atoms, cases that were excluded by Dunitz and co-workers;[31] in these examples the carbon was displaced towards the oxygen by 0.007 and 0.012 Å, respectively. In each of the structures (3a) and (3b), there was one short C=O · · · C=O interaction (2.68 and 2.64 Å), again separated by two intervening atoms. In these cases, the displacements of the carbon were 0.04 and 0.02 Å away from the interacting oxygen.

[33] L. J. Bellamy, ' The Infrared Spectra of Complex Molecules,' 2nd edn., Methuen, London, 1958.

acetonitrile solution are all red and have nearly identical visible spectra, in the solid the colours range from yellow, for (6b), to deep red, for the *p*-nitro-derivative (6d). Each of the compounds (6a—d) has absorptions in the 474 and in the 372 nm region. There are, however, different extinction coefficients for each compound, and also differences between solid and solution spectra. The ratios of the intensities of the two bands for (6a), (6b), and (6d) in acetonitrile solution and also in the solid state are given in Table 6. Interpretation of these differences in terms of the crystal structures is not possible at present.

TABLE 6

Spectral characteristics of some derivatives of indanetrione 2-(*N*-benzoyl-*N*-phenylhydrazone) in acetonitrile solution and in the solid state

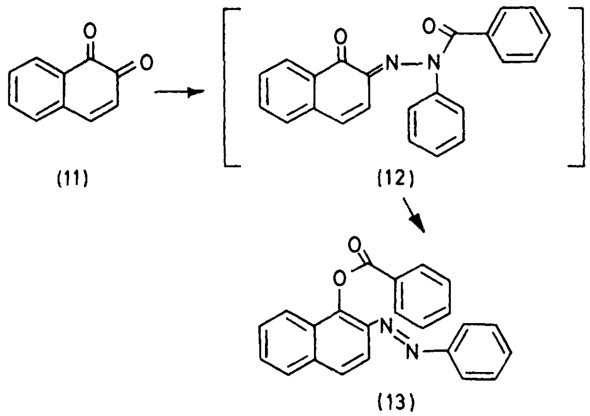
Compound	A_{474}/A_{372} solution	A_{474}/A_{372} solid state
(6a)	0.26	0.46
(6b)	0.28	0.33
(6d)	0.23	0.27

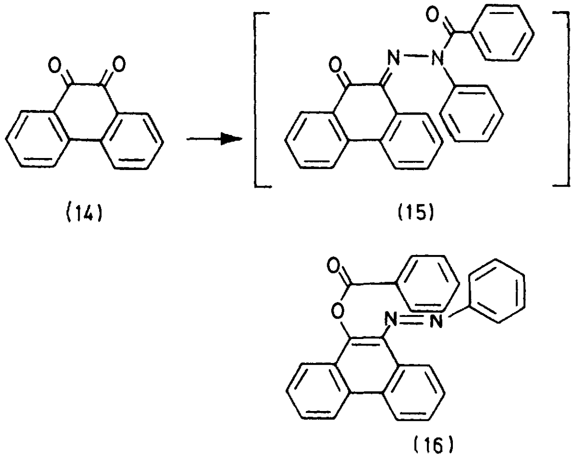
The 'Missing' Enol Benzoates (5).—Examination of reaction mixtures in which the benzoylhydrazones (6a—d) were being formed showed no indication of the enol benzoates (5). As was pointed out earlier, these compounds would, because of the constraint imposed by the five-membered ring, have the aroyloxy- and phenylazo-groups mutually *cis*, a configuration which should favour a ready rearrangement with O to N aroyl migration to give the observed products (6). Thus, the question arises whether, if the enol benzoates (5) were formed in the reaction studied here, they would undergo too rapid a rearrangement to (6) to permit their isolation or observation.

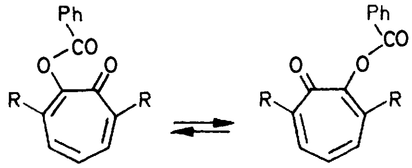
The *syn*-conformations of (6a) and (6b) are significant in this connection because the C(10)–O(2) geometry is nearly ideal for a rearrangement of (6) to (5), and it is suggested that the transition state for the reverse reaction (5) to (6), with similar geometry, should be highly favourable.

Evidence for rapid acyl migration in somewhat related systems has been reported.[34-38] For example, *N*-benzoyl-*N*-phenylhydrazine has been reported to react with 1,2-naphthoquinone (11) [39] to give, instead of the expected hydrazone (12), the product of acyl migration (13). Similarly, phenanthroquinone (14) gave (16).[40,41] Although these are N to O rearrangements their mechanisms are probably related to the O to N rearrangement of (5) to (6) being considered here. The equilibration of the tropolone esters (17) is rapid, even on the n.m.r. timescale at −110 °C.[42]

Crystal Packing of Indane-1,2,3-*trione* 2-(N-*Benzoyl*-N-*phenylhydrazone*) (6a).—Figure 4 shows a stereoscopic view of the molecular packing of (6a). There are no short intermolecular C=O···C=O interactions which appear to play an important role in determining the molecular arrangement in the crystal. The molecules of (6a) are arranged such that the indanedione rings form infinite stacks along the *c* direction, with planes being separated by 3.55 Å. This disposition of molecules also allows a partial overlap between centrosymmetrically related C(11)—(16) phenyl rings; the interplanar distance is 3.40 Å.


(11) (12) (13)


(14) (15) (16)



(17) (18)

Crystal Packing of Indane-1,2,3-*trione* 2-(N-p-*Bromobenzoyl*-N-*phenylhydrazone*) (6b).—The introduction of the bromo-substituent has altered substantially the crystal structure from that of (6a). There are two molecules of (6b) in the asymmetric unit, conformers

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[34] W. McPherson, *Amer. Chem. J.*, 1899, **22**, 381.

[35] R. Meldola and G. T. Morgan, *J. Chem. Soc.*, 1889, **55**, 606.

[36] H. Goldschmidt and R. Brubacher, *Ber.*, 1891, **24**, 2300.

[37] T. Zincke, *Ber.*, 1883, **16**, 1563.

[38] T. Zincke and H. Bindewald, *Ber.*, 1884, **17**, 3026.

[39] K. von Auwers and M. Eckardt, *Annalen*, 1908, **359**, 336.

[40] K. von Auwers, *Annalen*, 1911, **378**, 210.

[41] R. Ramart-Lucas, T. Guilmart, and M. Martynoff, *Bull. Soc. chim. France*, 1947, 415.

[42] V. I. Minkin, L. P. Olekhnovich, Yu. A. Zhdanov, Z. N. Budarina, and V. P. Metlushenko, *Tetrahedron Letters*, 1974, 563.

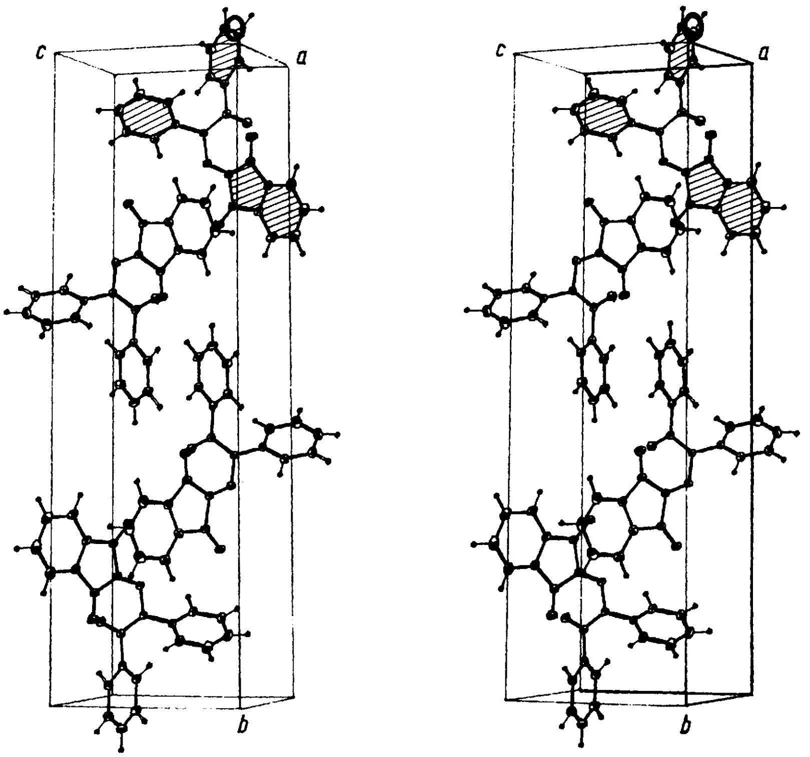

Figure 4 Stereoscopic packing of the crystal of (6a). The reference molecule is shaded

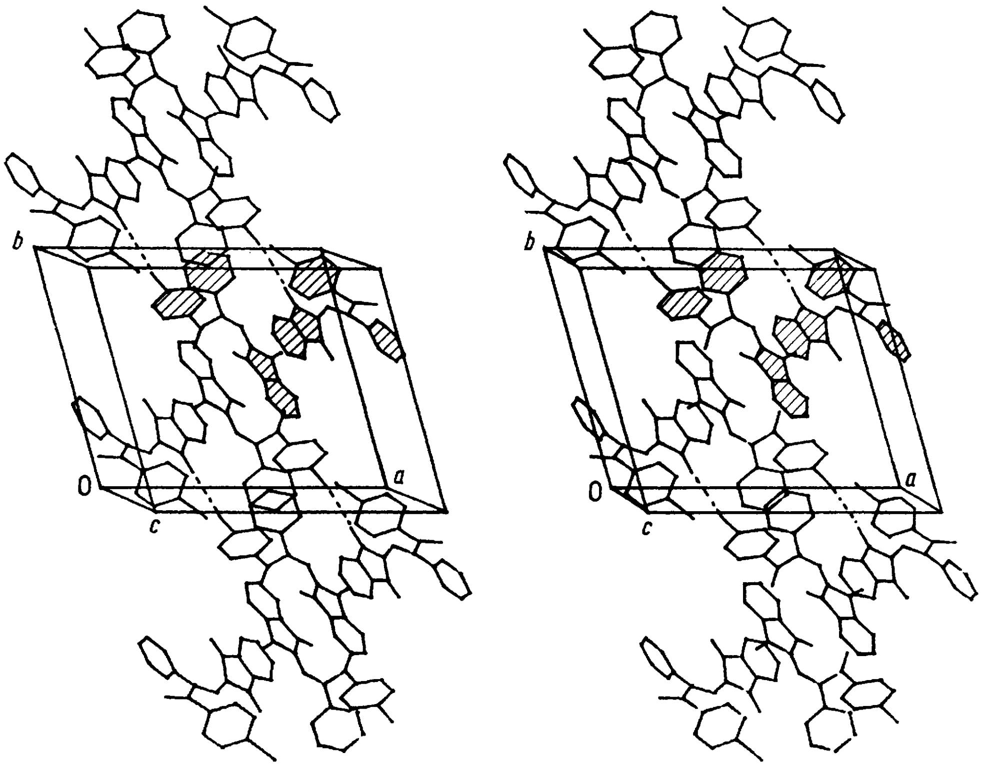

Figure 5 Stereoscopic view of the packing in the crystal of (6b) showing the Br · · · O interaction between pairs of *syn*- and *anti*-molecules along the *b* axis

related to each other by rotation about two single bonds, C(10)–N(2) and N(1)–N(2). It is comparatively rare to have two conformers in the same crystal, as packing forces are normally sufficient to provide a uniform conformation for molecules upon crystallization. Rotational isomers have been isolated, but as distinct and separate crystals, in cases where there are bulky substituents on the *ortho*-position of the phenyl rings attached to either the carbon or nitrogen atom of an amide group.[43–45]

The packing of (6b) is shown in Figure 5. The *syn*- and *anti*-rotamers of (6b) are linked by a Br(1) · · · O(2′) contact of 3.168 Å; this effective pairing of the two molecules may be responsible for the existence of the two rotamers in the crystal. This Br · · · O contact is significantly less than the sum of the van der Waals radii (3.35 Å).[46] The C(14)–Br(1) · · · O(2′) angle is 158 and C(3′)–O(2′) · · · Br(1) 137°. A survey of a number of halogen-containing carbonyl compounds reveals several instances (Table 7)[19,24,47–53] where there are short (*ca.* 3.3 Å) Br · · · O contacts which have important controlling influences on the packing of the molecules. The occurrence of such intermolecular bonding was recognised in a variety of halogen-substituted benzoquinones, naphthoquinones, and anthraquinones by Gaultier *et al.*,[54] who also identified Br(Cl) · · · O intermolecular interactions in both solution and the solid by i.r. spectroscopy. In the absence of other stronger intermolecular forces, such as hydrogen bonding, it appears that the Br · · · O interaction can be used as a starting point in determining the packing of compounds with a carbonyl group and a bromine atom. In the triclinic form of 2-(*p*-bromophenyl)indane-1,3-dione there are two independent molecules in the crystal asymmetric unit which participate in a Br · · · O intermolecular contact of 3.33 Å.[19] Somewhat similar Br · · · O contacts have been observed in a variety of molecular complexes,[55] *e.g.*, oxalyl bromide forms a 'self-complex'[56] with a Br · · · O contact of 3.27 Å and a stable 1 : 1 complex with other oxygen-containing molecules such as 1,4-dioxan with Br · · · O 3.21 Å.[57] On the basis of intermolecular distances in oxalyl bromide and chloride complexes, it appears that Br · · · O interactions have a greater effect upon crystal packing than Cl · · · O interactions.[54,55,58]

TABLE 7

Summary of intermolecular bromine–oxygen contacts (Å) in (6b) and certain related structures

Indane-1,2,3-trione 2-(N-*p*-bromobenzoyl-*N*-phenylhydrazone) (6b) [a]	3.168
Tribenzoyl-*p*-bromophenylazomethane (1b) [b]	3.22
2-(*p*-Bromophenyl)indane-1,3-dione [c] (triclinic)	3.33
2-Bromo-1,4-naphthoquinone [d]	3.10
2,3-Dibromo-1,4-naphthoquinone [e]	3.15
	3.22
2,5-Dibromo-1,4-benzoquinone [f]	3.16
3-Bromo-1,2-naphthoquinone [g]	3.17
Androsta-1,4,6-triene-3,17-dione–*p*-bromophenol complex [h]	3.22
N-(*p*-Bromophenyl)sydnone [i]	3.16
syn-*p*-Bromobenzophenone *O*-picryloxime [j]	3.30

[a] This work. [b] Ref. 24. [c] Ref. 19. [d] Ref. 47. [e] Ref. 48. Ref. 49. [g] Ref. 50. [h] Ref. 51. [i] Ref. 52. [j] Ref. 53.

In addition to the Br · · · O contact, there are also two Br · · · Br contacts which appear significant. The first of these [$\mathrm{Br}(1') \cdots \mathrm{Br}(1'^{\mathrm{I}})$ 4.03 Å] occurs between the bromine in the reference *anti*-(6b) molecule and the bromine in the *anti*-(6b) molecule at $2 - x$, $2 - y$, $-1 - z$; the $\mathrm{C}(14')\text{–}\mathrm{Br}(1') \cdots \mathrm{Br}(1'^{\mathrm{I}})$ $(2 - x,\ 2 - y,\ -1 - z)$ angle is 92°. The second contact [$\mathrm{Br}(1) \cdots \mathrm{Br}(1'^{\mathrm{II}})$ 3.94 Å] is between the reference *syn*-molecule and the *anti*-molecule at $1 - x$, $2 - y$, $-z$; the $\mathrm{C}(14)\text{–}\mathrm{Br}(1) \cdots \mathrm{Br}(1'^{\mathrm{II}})$ angle is 109 and $\mathrm{Br}(1) \cdots \mathrm{Br}(1'^{\mathrm{II}})\text{–}\mathrm{C}(14'^{\mathrm{II}})$ 160°. Other Br · · · Br contacts less than twice the van der Waals radius have been noted when the C–Br · · · Br angle approaches linearity.[59,60] The significance of such halogen–halogen interactions in influencing packing arrangements has been noted previously.[13,61,62] There is also an overlap of indane rings between the two independent molecules somewhat similar to that found in (6a) with a plane-to-plane separation of 3.42 Å; the angle between the planes is 5.4°.

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[43] T. H. Siddall III and R. H. Garner, *Canad. J. Chem.*, 1966, **44**, 2387.

[44] H. A. Staab and D. Lauer, *Tetrahedron Letters*, 1966, 4593.

[45] J. P. Chupp and J. F. Olin, *J. Org. Chem.*, 1967, **32**, 2297.

[46] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, pp. 257—264.

[47] J. Gaultier and C. Hauw, *Acta Cryst.*, 1965, **18**, 604.

[48] M. Breton-Lacombe, *Acta Cryst.*, 1967, **23**, 1031.

[49] B. Rees, R. Haser, and R. Weiss, *Bull. Soc. chim. France*, 1966, 2658.

[50] C. Courseille, J. Gaultier, C. Hauw, and M. Schvoerer, *Compt. rend.*, 1970, **C270**, 687.

[51] D. N. Peck, D. A. Langs, C. Eger, and W. L. Duax, *Cryst. Struct. Comm.*, 1974, **3**, 451.

[52] H. Bärnighausen, F. Jellinek, J. Munnik, and A. Vos, *Acta Cryst.*, 1963, **16**, 471.

[53] J. D. McCullough, jun., I. C. Paul, and D. Y. Curtin, *J. Amer. Chem. Soc.*, 1972, **94**, 883.

[54] J. Gaultier, C. Hauw, and M. Schvoerer, *Acta Cryst.*, 1971, **B27**, 2199.

[55] C. K. Prout and B. Kamenar, in 'Molecular Complexes,' ed. R. Foster, vol. 1, Crane, Russak, New York, 1973.

[56] P. Groth and O. Hassel, *Acta Chem. Scand.*, 1962, **16**, 2311.

[57] E. Damm, O. Hassel, and C. Rømming, *Acta Chem. Scand.*, 1965, **19**, 1159.

[58] L. J. Andrews and R. M. Keefer, 'Molecular Complexes in Organic Chemistry,' Holden Day, San Francisco, 1964, pp. 49—55.

[59] M. G. Newton, M. C. McDaniel, J. E. Baldwin, and I. C. Paul, *J. Chem. Soc., B*, 1967, 1117.

[60] J. A. McMillan and I. C. Paul, *Cryst. Struct. Comm.*, 1975, **4**, 445.

[61] T. Sakurai, M. Sundaralingam, and G. A. Jeffrey, *Acta Cryst.*, 1963, **16**, 354.

[62] R. S. Miller, D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.*, 1974, **96**, 6340.