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Indan-1,2,3-trione 2-(*N*-*p*-*tert*-Butylbenzoyl-*N*-phenylhydrazone)

BY REGINALD A. BOOKER, DAVID Y. CURTIN AND IAIN C. PAUL

Department of Chemistry, University of Illinois, Urbana, Illinois 61801, *USA*

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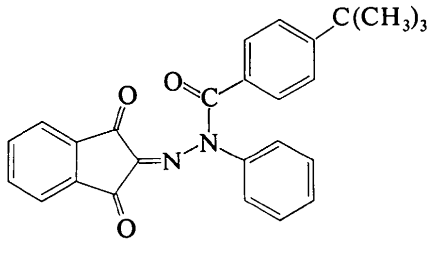
Abstract. $C_{26}H_{22}N_2O_3$, M_r = 410·5, triclinic, space group $P\bar{1}$, a = 10·076 (7), b = 11·854 (6), c = 10·463 (5) Å, α = 99·61 (4), β = 115·29 (4), γ = 87·75 (5)°, $V = 1113{\cdot}4 \times 10^{-24}$ cm³, $Z = 2$, $D_c = 1{\cdot}22$ g cm^{-3}, μ(Cu $K\alpha$) = 6·6 cm^{-1}. The X-ray analysis (R = 0·071 on 2935 reflections) provides the crystal structure of the form of indan-1,2,3-trione 2-(*N*-*p*-*tert*-butylbenzoyl-*N*-phenylhydrazone) that is obtained by crystallization from ethyl ether/isooctane.

Introduction. When indan-1,2,3-trione 2-(*N*-*p*-*tert*-butylbenzoyl-*N*-phenylhydrazone) (1) is crystallized from acetone, orange crystals (m.p. 160–165 °C) of a 1 : 1 acetone solvent of (1) are obtained (Puckett, 1975). The crystal structure of this acetone solvate has been determined and the course of loss of acetone from the crystals has been investigated (Puckett, Paul & Curtin, 1976). X-ray powder patterns of the material left after loss of acetone show that this red material has a different crystal structure from the red solvent-free crystals (m.p. 159–161 °C) obtained by crystallization from ethyl ether/isooctane mixtures. The present paper reports the crystal structure of the red solvent-free crystals. Cell data were obtained from a least-squares fit to the 2θ settings for thirteen reflections centered on a Syntex $P2_1$ diffractometer (λ = 1·5418 Å, ambient room temperature). Intensity data to a maximum 2θ of 130° were collected on a Syntex $P2_1$ diffractometer using a continuous 2θ-scan procedure; scan speeds ranged from 2–10° min^{-1}. A total of 2935 reflections out of a possible 3784 were considered non-zero at the 1·96σ level of significance. No corrections were applied for absorption or extinction. The structure was solved by the use of the *MULTAN* direct methods program (Germain, Main & Woolfson, 1971) that is incorporated in the Syntex *EXTL* system. Refinement was carried out by block-diagonal and finally by full-matrix least-squares methods using the programs in the *EXTL* system. All hydrogen atoms except those for the *tert*-butyl group were located from a difference map. The hydrogen atoms for the *tert*-butyl group could not be located with certainty and were not included in the model. The final values of R and R_w $[(\sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}]$ for the non-zero reflections are 0·071 and 0·099; the 'goodness of fit' is 3·00. Scattering factors were those from *International Tables for X-ray Crystallography* (1974). The final atomic coordinates are listed in Table 1.*



(1)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33555 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates for* (1)

	x	*y*	*z*
C(1)	0·7774 (4)	0·6240 (3)	0·9523 (4)
C(2)	0·6889 (4)	0·7074 (3)	0·8581 (4)
C(3)	0·7872 (4)	0·8100 (3)	0·8908 (4)
C(4)	0·9323 (4)	0·7858 (3)	1·0037 (4)
C(5)	1·0603 (5)	0·8521 (4)	1·0727 (5)
C(6)	1·1804 (5)	0·8098 (4)	1·1753 (5)
C(7)	1·1720 (5)	0·7048 (4)	1·2084 (6)
C(8)	1·0450 (4)	0·6379 (4)	1·1427 (4)
C(9)	0·9254 (4)	0·6789 (3)	1·0393 (4)
C(10)	0·5166 (4)	0·5067 (3)	0·6892 (3)
C(11)	0·4405 (3)	0·3992 (3)	0·6772 (3)
C(12)	0·4322 (4)	0·3082 (3)	0·5718 (4)
C(13)	0·3845 (4)	0·2006 (3)	0·5695 (4)
C(14)	0·3439 (4)	0·1784 (3)	0·6739 (4)
C(15)	0·3499 (5)	0·2704 (3)	0·7778 (5)
C(16)	0·3959 (4)	0·3794 (3)	0·7802 (4)
C(17)	0·3143 (4)	0·6310 (3)	0·6998 (4)
C(18)	0·2680 (5)	0·6775 (5)	0·8016 (5)
C(19)	0·1218 (7)	0·7015 (6)	0·7598 (8)
C(20)	0·0226 (6)	0·6800 (5)	0·6173 (8)
C(21)	0·0692 (5)	0·6339 (5)	0·5187 (6)
C(22)	0·2164 (4)	0·6087 (4)	0·5591 (5)
C(23)	0·2971 (5)	0·0578 (3)	0·6787 (5)
C(24)	0·4116 (9)	0·0192 (6)	0·8178 (10)
C(25)	0·2848 (11)	−0·0278 (5)	0·5531 (9)
C(26)	0·1514 (8)	0·0626 (5)	0·6904 (8)
O(1)	0·7339 (3)	0·5338 (2)	0·9637 (3
O(2)	0·7557 (3)	0·8941 (2)	0·8328 (4)
O(3)	0·6201 (3)	0·5083 (2)	0·6598 (2)
N(1)	0·5505 (3)	0·7112 (2)	0·7781 (3)
N(2)	0·4686 (3)	0·6098 (2)	0·7435 (3)
H(5)(a)	1·069 (5)	0·916 (4)	1·063 (5)
H(6)	1·279 (5)	0·849 (4)	1·233 (5)
H(7)	1·243 (5)	0·676 (4)	1·266 (5)
H(8)	1·034 (4)	0·561 (3)	1·164 (4)
H(12)	0·451 (5)	0·314 (4)	0·499 (5)
H(13)	0·383 (4)	0·141 (3)	0·497 (4)
H(15)	0·303 (4)	0·266 (3)	0·838 (4)
H(16)	0·397 (4)	0·436 (3)	0·852 (4)
H(18)(b)	0·336	0·689	0·903
H(19)(b)	0·085	0·730	0·826
H(20)	−0·091 (6)	0·700 (5)	0·567 (6)
H(21)	−0·010 (6)	0·608 (4)	0·401 (6)
H(22)	0·235 (5)	0·574 (4)	0·487 (5)

(*a*) Hydrogen atoms were given the numbers of the atoms to which they are attached.

(*b*) The atomic coordinates for these hydrogen atoms were not varied in the refinement.

Table 2. *Bond lengths* (Å) *and angles* (°) *in* (1)

The C—H lengths range from 0·80 (4) to 1·14 (5) Å.

C(1)—C(2)	1·500 (5)	C(10)—O(3)	1·207 (5)
C(1)—C(9)	1·481 (4)	C(11)—C(12)	1·385 (5)
C(1)—O(1)	1·214 (4)	C(11)—C(16)	1·388 (6)
C(2)—C(3)	1·497 (5)	C(12)—C(13)	1·373 (5)
C(2)—N(1)	1·288 (5)	C(13)—C(14)	1·385 (6)
C(3)—C(4)	1·490 (6)	C(14)—C(15)	1·388 (6)
C(3)—O(2)	1·215 (5)	C(15)—C(16)	1·383 (6)
C(4)—C(9)	1·392 (5)	C(17)—C(18)	1·366 (7)
C(4)—C(5)	1·377 (7)	C(17)—C(22)	1·364 (6)
C(5)—C(6)	1·375 (7)	C(18)—C(19)	1·379 (9)
C(6)—C(7)	1·361 (7)	C(19)—C(20)	1·381 (10)
C(7)—C(8)	1·373 (7)	C(20)—C(21)	1·338 (9)
C(8)—C(9)	1·370 (6)	C(21)—C(22)	1·393 (8)
N(1)—N(2)	1·391 (4)	C(14)—C(23)	1·538 (5)
N(2)—C(10)	1·417 (4)	C(23)—C(24)	1·550 (10)
N(2)—C(17)	1·445 (4)	C(23)—C(25)	1·483 (9)
C(10)—C(11)	1·473 (5)	C(23)—C(26)	1·522 (10)

C(2)—C(1)—C(9)	106·1 (3)	C(11)—C(10)—O(3)	122·2 (3)
C(2)—C(1)—O(1)	127·1 (3)	C(10)—C(11)—C(12)	119·1 (3)
C(9)—C(1)—O(1)	126·5 (3)	C(10)—C(11)—C(16)	122·3 (3)
C(1)—C(2)—C(3)	107·3 (3)	C(12)—C(11)—C(16)	118·0 (3)
C(1)—C(2)—N(1)	132·2 (3)	C(11)—C(12)—C(13)	121·7 (4)
C(3)—C(2)—N(1)	119·6 (3)	C(12)—C(13)—C(14)	121·1 (4)
C(2)—C(3)—C(4)	106·3 (3)	C(13)—C(14)—C(15)	116·9 (4)
C(2)—C(3)—O(2)	126·5 (4)	C(13)—C(14)—C(23)	122·5 (4)
C(4)—C(3)—O(2)	127·1 (4)	C(15)—C(14)—C(23)	120·6 (4)
C(3)—C(4)—C(9)	109·7 (3)	C(14)—C(15)—C(16)	122·5 (4)
C(3)—C(4)—C(5)	130·1 (4)	C(11)—C(16)—C(15)	119·7 (4)
C(5)—C(4)—C(9)	120·2 (4)	N(2)—C(17)—C(18)	118·8 (4)
C(4)—C(5)—C(6)	118·7 (5)	N(2)—C(17)—C(22)	121·1 (4)
C(5)—C(6)—C(7)	120·4 (5)	C(18)—C(17)—C(22)	120·1 (4)
C(6)—C(7)—C(8)	122·0 (5)	C(17)—C(18)—C(19)	119·0 (5)
C(7)—C(8)—C(9)	117·9 (4)	C(18)—C(19)—C(20)	121·1 (6)
C(1)—C(9)—C(4)	110·5 (3)	C(19)—C(20)—C(21)	119·3 (6)
C(1)—C(9)—C(8)	128·7 (4)	C(20)—C(21)—C(22)	120·4 (6)
C(4)—C(9)—C(8)	120·8 (4)	C(17)—C(22)—C(21)	120·1 (5)
C(2)—N(1)—N(2)	116·2 (3)	C(14)—C(23)—C(24)	108·2 (5)
N(1)—N(2)—C(10)	119·7 (3)	C(14)—C(23)—C(25)	113·3 (5)
N(1)—N(2)—C(17)	111·4 (3)	C(14)—C(23)—C(26)	109·5 (4)
C(10)—N(2)—C(17)	121·6 (3)	C(24)—C(23)—C(25)	109·4 (6)
N(2)—C(10)—C(11)	117·5 (3)	C(24)—C(23)—C(26)	106·4 (5)
N(2)—C(10)—O(3)	120·3 (3)	C(25)—C(23)—C(26)	109·8 (5)

Discussion. A stereoscopic view of the molecular structure of (1) is shown in Fig. 1. Bond lengths and angles are given in Table 2. The molecular dimensions in (1) are similar to those in other members of the series (Puckett, Greensley, Paul & Curtin, 1977; McMillan, Curtin & Paul, 1978). Of particular interest are the large thermal vibrations of the *tert*-butyl group and of the phenyl ring [C(17)–C(22)]. In the 1:1 acetonate (Puckett, Paul & Curtin, 1976), the *tert*-butyl group exhibited disorder by occupying two sites differing by rotation of 60° about the C(aromatic)—C(*tert*-butyl) bond, but there was no evidence for large thermal movement of the C(17)–C(22) phenyl ring. In (1), refinement of a model with two sites for the terminal carbon atoms of the *tert*-butyl group resulted in a model in which the two sites converged. In contrast to the case of the 1:1 acetonate, the structure of (1) is better represented by a single rotamer model for the *tert*-butyl group with considerable oscillation about the C(14)—C(23) bond.

A stereoscopic view of the packing of (1) is shown in Fig. 2. A comparison of the packing of (1) in the crystal by itself and as the 1:1 acetonate is shown in Fig. 3. It is seen that in each structure there is a double layer of molecules in which molecules are related by centers of symmetry. In the crystal of (1) these layers are simply repeated in the *b* direction. However, in the acetonate (Puckett, Paul & Curtin, 1976), channels of acetone

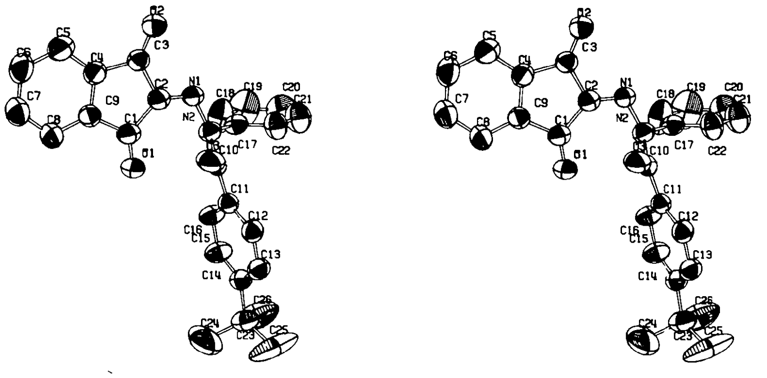


Fig. 1. Stereoscopic view of a single molecule of (1).

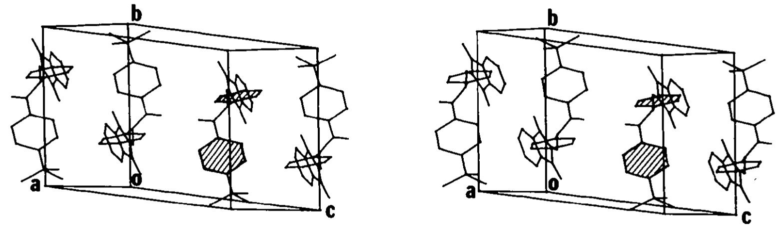
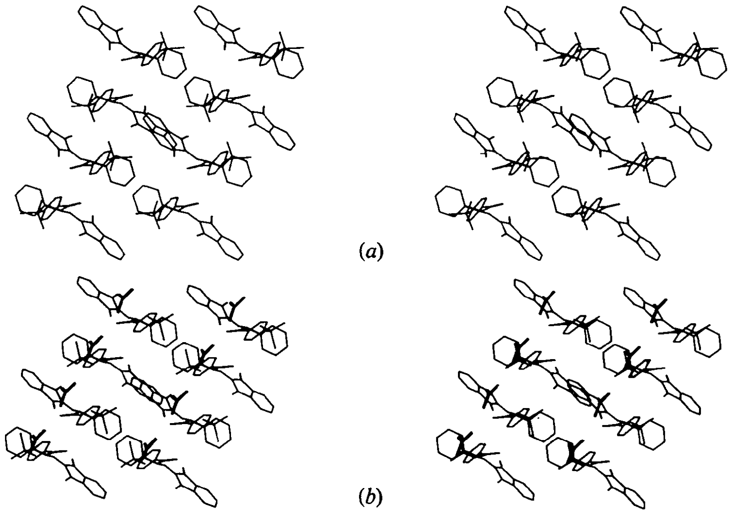


Fig. 2. Packing of (1) in the crystal. The reference molecule has the two phenyl rings shaded.



(*a*)

(*b*)

Fig. 3. (*a*) View of the packing of (1) looking onto the *ac* plane. The *c* axis runs diagonally to the left and the *a* axis runs horizontally to the right. (*b*) View of the packing of molecule (1) in the 1:1 acetone complex. The *c* direction runs diagonally to the left and [101] runs horizontally to the right. The *tert*-butyl group is shown arbitrarily in one of the two conformations it assumes in the disordered structure. Only one half of the structure is shown. Molecules of (1) of types x,y,z and $\bar{x},\bar{y},\bar{z}$ and acetone molecules of types x,y,z and $x, y+\frac{1}{2}, \frac{1}{2}-z$ form this layer. A second symmetry-related layer not shown, but which would be closer to the viewer, completes the structure. The acetone molecules are shown by heavy lines in (*b*).

molecules are found running in a diagonal direction shown in Fig. 3(*b*). The 1:1 acetonate crystallizes in the space group $P2_1/c$ with four molecules of (1) in the cell. In that structure the acetone molecules were held quite tightly in essentially separate compartments of the channel. One of the walls of these compartments consisted of the C(17)–C(22) phenyl ring. Apparently the absence of the channel of acetone molecules has resulted in more flexibility and freedom of motion for this ring in (1) as can be seen in Fig. 1. On the side of the C(17)–C(22) ring opposite to where the hypothetical acetone channel would be in the crystal of (1), there is a short intermolecular contact of 3·41 Å between C(21) and the C(21) atom in the molecule at

$-x$, $1 - y$, $1 - z$. This short contact at one point in the ring may be responsible for the non-symmetrical thermal motion of the ring.

We thank Dr S. A. Puckett for providing a precursor of (1) used in this study. We acknowledge support for R. A. Booker from NIH and NSF.

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(±)-2-(3,5-Dichlorophenoxy)propanoic Acid*

BY GRAHAM SMITH

Department of Chemistry, Queensland Institute of Technology, Brisbane, Queensland 4000, *Australia*

COLIN H. L. KENNARD

Department of Chemistry, University of Queensland, Brisbane, Queensland 4067, *Australia*

AND ALLAN H. WHITE

Department of Physical and Inorganic Chemistry, University of Western Australia, Perth, Western Australia 6009, *Australia*

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Abstract. $C_9H_8Cl_2O_3$, triclinic, $P\bar{1}$, $a = 9{\cdot}615\,(4)$, $b = 8{\cdot}503\,(3)$, $c = 7{\cdot}505\,(3)$ Å, $\alpha = 114{\cdot}36\,(3)$, $\beta = 106{\cdot}62\,(3)$, $\gamma = 97{\cdot}37\,(3)^\circ$, $M_r = 235{\cdot}1$, $Z = 2$, $D_x = 1{\cdot}52$ g cm^{-3}, $\mu(\text{Mo } K\alpha) = 6{\cdot}09$ cm^{-1}; $R = 0{\cdot}065$, 1168 reflections. The molecules form synplanar hydrogen-bonded cyclic dimers. The molecular conformation is very similar to that observed in (±)-2-(2,4,5-trichlorophenoxy)propanoic acid (2,4,5-TP) with the dihedral angle between the planes of the benzene ring and the carboxylic acid group being 87·0° (2,4,5-TP = 77·8°). The distance between the carboxylic acid O atom and C(2) of the aromatic ring (3·68 Å) is short compared with those in other members of the phenoxyalkanoic acid series.

Introduction. The title compound (3,5-DP) is a member of the series of commercially important synthetic auxin herbicides which include 2,4-D (2,4-dichlorophenoxyacetic acid), 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) and Fenoprop [(±)-2-(2,4,5-trichlorophenoxy)propanoic acid (2,4,5-TP)], the structures of which have been described (Smith, Kennard, White & Hodgson, 1977). Some herbicidally inactive members of the series of chloro-substituted phenoxyacetic acids are the 2,4,6-trichloro (2,4,6-T) and 3,5-dichloro (3,5-D) analogues. The structure of 2,4,6-T has been determined (Smith, Kennard & White, 1977) but the growing of suitable crystals of 3,5-D has so far proved impossible. Since activity in the propanoic acid series usually parallels the acetic acid series with respect to ring chlorine substitution, the structure of 3,5-DP was investigated. The compound was prepared by the interaction of ethyl 2-bromopropanoate with sodium 3,5-dichlorophenoxide (Synerholm & Zimmerman, 1945). White crystals were grown from a mixture of toluene and chloroform. 1168 reflections with $|F_o| > 2{\cdot}5|\sigma(F_o)|$ were considered observed out of 1800 collected from a crystal (0·5 × 0·35 × 0·15 mm) mounted on a Syntex $P\bar{1}$ four-circle diffractometer ($2\theta_{\max} = 50^\circ$) using graphite-monochromated Mo $K\alpha$ radiation. No absorption corrections were made [$\mu(\text{Mo } K\alpha) = 6{\cdot}09$ cm^{-1}].

The structure was solved by multisolution $\sum_2$ sign expansion (Sheldrick, 1976). Full-matrix least-squares refinement with anisotropic temperature factors on all

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* Herbicides. VI. Part V: Smith, Kennard, White & Hodgson (1977).