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Structure of 2-(2-Nitrobenzylidene)indan-1,3-dione

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Abstract. $C_{16}H_9NO_4$, M_r=279·251, monoclinic, $P2_1/a$, a = 7·446 (5), b = 13·958 (7), c = 12·635 (5) Å, β = 105·28 (7)°, V = 1266·75 Å^3, Z = 4, D_x = 1·464 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 0·65 mm^{-1}, $F(000)$ = 576, T = 293 K, R = 0·043 for 1189 reflections. The nitrobenzylidene fragment is tilted by ~40° from the plane of the indan-1,3-dione fragment. Intermolecular contacts are between similar fragments, ruling out the possibility of photosemiconductivity by electron charge transfer in crystals of the title compound.

Introduction. The crystal structures of a number of derivatives of indan-1,3-dione have been studied over the last ten years on account of the well-known anticoagulant activity of this compound in the vitamin K dependent biosynthesis (Ernster, Lind & Rase, 1972; Bravic, Gaultier & Hauw, 1974*a,b*; Csöregh & Eckstein, 1979). Some of the derivatives such as 2-dicyanomethyleneindan-1,3-dione (Silverman, Krukonis & Yannoni, 1974) have also been shown to be charge-transfer complexes. The present study is part of a programme of crystal structure analysis of some new derivatives of indan-1,3-dione.

Experimental. The title compound was synthesized by Lankin & Zimmer (1972) by reacting indan-1,3-dione with 2-nitrobenzaldehyde in glacial acetic acid containing a small fraction of concentrated sulfuric acid. Plate-shaped crystals were obtained by recrystallization from ethanol.

Approximate crystal dimensions: 0·35 × 0·10 × 0·60 mm. Enraf–Nonius CAD-4 automated diffractometer; graphite monochromator. Cell parameters refined by least-squares method on the basis of 25 2θ values ($2 < 2\theta < 40°$). No significant variation in intensities of two check reflections, monitored every 100 reflections. Lp correction. Absorption neglected, 1854 unique reflections with $2 < 2\theta < 40°$ (*hkl* range: $h\pm7$, $k\pm14$, $l\pm13$); 1189 with $I > 3\sigma(I)$. Structure solved by multisolution technique using *MULTAN*80 (Main *et al.*, 1980). Refinement (on *F*) by the least-squares method with *SHELX*76 (Sheldrick, 1976). H-atom positions from difference Fourier map at intermediate stage. Final *R* value with anisotropic thermal parameters for the non-H atoms and individual isotropic thermal parameters for the H atoms with unit weights is R = 0·043. Max. Δ/σ = 0·0382; max. and min. heights in final difference Fourier synthesis, 0·22 and −0·35 e Å^{-3}. Scattering factors from *SHELX*76.

Discussion. The atomic coordinates are listed in Table 1. An *ORTEP* plot (Johnson, 1965) of the molecule is shown in Fig. 1. The bond distances and the bond angles are listed in Table 2.†

The sp^2–sp^2 bond lengths of the five-membered ring C(1)···C(9), which vary from 1·474 (8) to 1·487 (7) Å, exhibit internal consistency, equivalent bonds having equal lengths within their e.s.d.'s. However, these bonds assume different values in different derivatives of

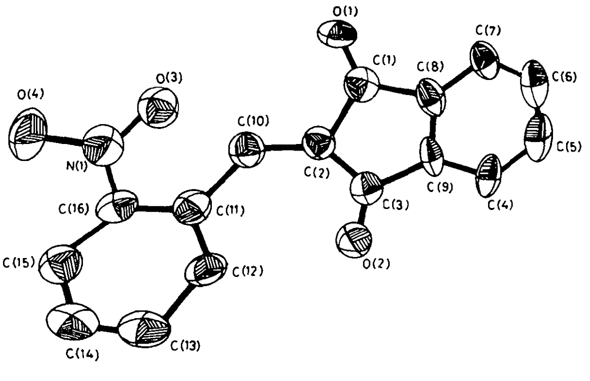

Fig. 1. *ORTEP* plot of the molecule showing the thermal ellipsoids drawn at 50% probability.

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† Lists of structure factors, selected torsion angles, details of least-squares planes, intermolecular contact distances, and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43081 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final fractional atomic coordinates* ($\times 10^4$ *for non*-H *atoms*; $\times 10^3$ *for* H *atoms*) *with e.s.d.'s in parentheses*

$$U_{\text{eq}} = \sum_{i=1}^{3} U_{ii}/3.$$

	x	y	z	$U_{\text{eq}}(\times 10^3 \text{Å}^2)$
C(1)	3900 (8)	2263 (4)	1525 (4)	46 (4)
C(2)	4469 (8)	3181 (4)	2111 (4)	42 (3)
C(3)	3481 (9)	3965 (5)	1416 (4)	47 (4)
C(4)	1317 (10)	3946 (6)	−559 (5)	63 (5)
C(5)	452 (11)	3339 (7)	−1408 (6)	72 (6)
C(6)	618 (10)	2365 (7)	−1327 (5)	72 (6)
C(7)	1697 (10)	1929 (6)	−403 (5)	64 (5)
C(8)	2610 (8)	2523 (5)	453 (4)	50 (4)
C(9)	2412 (9)	3510 (5)	382 (4)	49 (4)
C(10)	5653 (8)	3181 (4)	3119 (4)	44 (3)
C(11)	6418 (8)	4002 (4)	3825 (4)	41 (3)
C(12)	7040 (9)	4821 (4)	3401 (5)	51 (4)
C(13)	7817 (9)	5576 (5)	4072 (7)	60 (5)
C(14)	7994 (9)	5527 (5)	5181 (6)	57 (5)
C(15)	7429 (9)	4731 (5)	5626 (5)	51 (4)
C(16)	6635 (8)	3993 (4)	4959 (4)	40 (3)
N(1)	5979 (7)	3164 (4)	5458 (4)	49 (3)
O(1)	4383 (6)	1462 (3)	1852 (3)	61 (3)
O(2)	3447 (7)	4814 (3)	1629 (3)	70 (3)
O(3)	4708 (6)	2629 (3)	4912 (3)	62 (3)
O(4)	6708 (7)	3011 (4)	6429 (3)	77 (3)
H(4)	96 (10)	471 (5)	365 (5)	99 (27)
H(5)	−19 (10)	364 (5)	−198 (6)	92 (25)
H(6)	5 (8)	197 (4)	−188 (5)	66 (18)
H(7)	186 (9)	120 (5)	−36 (5)	88 (21)
H(10)	615 (8)	250 (5)	347 (4)	68 (19)
H(12)	691 (12)	481 (6)	252 (7)	144 (35)
H(13)	818 (9)	627 (5)	381 (5)	80 (23)
H(14)	851 (9)	611 (5)	554 (5)	57 (21)
H(15)	752 (7)	466 (4)	630 (4)	61 (17)

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

C(1)—C(2)	1·485 (8)	C(12)—C(13)	1·381 (9)
C(1)—C(8)	1·487 (7)	C(13)—C(14)	1·377 (11)
C(1)—O(1)	1·213 (7)	C(14)—C(15)	1·361 (10)
C(2)—C(3)	1·474 (8)	C(15)—C(16)	1·364 (8)
C(2)—C(10)	1·347 (7)	C(16)—N(1)	1·463 (8)
C(3)—C(9)	1·484 (7)	N(1)—O(3)	1·227 (6)
C(3)—O(2)	1·217 (8)	N(1)—O(4)	1·225 (6)
C(4)—C(5)	1·387 (11)	C(4)—H(4)	1·107 (7)
C(4)—C(9)	1·394 (8)	C(5)—H(5)	0·86 (7)
C(5)—C(6)	1·367 (14)	C(6)—H(6)	0·90 (5)
C(6)—C(7)	1·375 (9)	C(7)—H(7)	1·02 (7)
C(7)—C(8)	1·391 (9)	C(10)—H(10)	1·07 (7)
C(8)—C(9)	1·386 (10)	C(12)—H(12)	1·09 (9)
C(10)—C(11)	1·473 (7)	C(13)—H(13)	1·08 (7)
C(11)—C(12)	1·393 (9)	C(14)—H(14)	0·96 (6)
C(11)—C(16)	1·402 (7)	C(15)—H(15)	0·84 (5)

C(1)—C(2)—C(3)	108·1 (4)	C(12)—C(13)—C(14)	120·1 (5)
C(1)—C(2)—C(10)	120·2 (4)	C(13)—C(14)—C(15)	120·4 (5)
C(2)—C(1)—C(8)	106·0 (4)	C(14)—C(15)—C(16)	119·4 (5)
C(1)—C(8)—C(7)	129·2 (5)	C(15)—C(16)—N(1)	118·0 (4)
C(1)—C(8)—C(9)	109·5 (4)	C(16)—N(1)—O(3)	119·9 (4)
C(2)—C(1)—O(1)	127·2 (4)	C(16)—N(1)—O(4)	117·5 (4)
C(8)—C(1)—O(1)	126·8 (4)	O(3)—N(1)—O(4)	122·6 (4)
C(2)—C(3)—C(9)	106·1 (4)	C(2)—C(10)—H(10)	117 (2)
C(2)—C(3)—O(2)	128·8 (4)	C(4)—C(5)—H(5)	113 (3)
C(3)—C(2)—C(10)	131·7 (4)	C(5)—C(4)—H(4)	117 (2)
C(2)—C(10)—C(11)	128·9 (4)	C(9)—C(4)—H(4)	126 (2)
C(3)—C(9)—C(4)	128·6 (5)	C(5)—C(6)—H(6)	122 (2)
C(3)—C(9)—C(8)	110·2 (4)	C(6)—C(5)—H(5)	124 (3)
C(9)—C(3)—O(2)	125·1 (4)	C(6)—C(7)—H(7)	121 (3)
C(4)—C(5)—C(6)	122·4 (6)	C(7)—C(6)—H(6)	116 (2)
C(5)—C(4)—C(9)	116·3 (5)	C(8)—C(7)—H(7)	122 (3)
C(4)—C(9)—C(8)	121·2 (5)	C(11)—C(10)—H(10)	114 (2)
C(5)—C(6)—C(7)	121·7 (6)	C(11)—C(12)—H(12)	115 (3)
C(6)—C(7)—C(8)	117·1 (5)	C(12)—C(13)—H(13)	126 (2)
C(7)—C(8)—C(9)	121·3 (5)	C(13)—C(12)—H(12)	123 (3)
C(10)—C(11)—C(12)	121·3 (4)	C(13)—C(14)—H(14)	111 (2)
C(10)—C(11)—C(16)	122·5 (4)	C(14)—C(13)—H(13)	113 (2)
C(11)—C(12)—C(13)	121·1 (5)	C(14)—C(15)—H(15)	124 (2)
C(12)—C(11)—C(16)	116·2 (4)	C(15)—C(14)—H(14)	129 (2)
C(11)—C(16)—C(15)	122·8 (4)	C(16)—C(15)—H(15)	116 (2)
C(11)—C(16)—N(1)	119·2 (4)		

indan-1,3-dione [*e.g.*, 2-dicyanomethyleneindan-1,3-dione (Silverman, Krukonis & Yannoni, 1974) with distances varying from 1·475 to 1·505 Å], depending on the chemical environments resulting from the nature of the substituents. The C(2)—C(10) bond, linking indan-1,3-dione with the substituent, assumes values longer than the C=C bond distance (1·33 Å) depending on the degree of resonance. It is 1·347 (7) Å in the title compound. The C(aromatic)—N distance [1·463 (8) Å] agrees with values usually reported for this bond, as, for example, in 4-bromo-1-(4-nitrophenyl)-3-phenylpyridazinium-5-olate [1·473 (3) Å] (Caristi, Gattuso, D'Alcontres, Ferlazzo, Bart & Day, 1983) and bis(cyclohexylammonium) 4-nitrophenyl phosphate dihydrate [1·471 (10) Å] (Jones & Sheldrick, 1984).

The small contraction of the aromatic angles C(6)—C(7)—C(8) and C(5)—C(4)—C(9) (~3°) and the small expansion of the *ipso* angles C(4)—C(9)—C(8) and C(7)—C(8)—C(9) are common features of benzene rings fused to small rings and have been explained by simple force-field calculations of angle bending strains by Allen (1981).

The rotation of the ring C(11)···C(16) from the plane of the indan-1,3-dione fragment (~40°) is attributed to the steric repulsion between the nonbonded atoms O(2) and C(12), which are only 2·99 Å apart. Likewise, the tilt of the plane of the nitro group from the plane of the ring C(11)···C(16) (~25°) can be traced to the repulsive interaction between the nonbonded atoms C(15) and O(4), which are only 2·71 Å apart.

The conjugated chain of bonds, C(2)=C(10)—C(11)=C(16), linking the donor indan-1,3-dione fragment with the acceptor nitrobenzylidene fragment indicates the possibility of intramolecular charge transfer.

However, the possibility of the presence of similar charge transfer between the acceptor and donor fragments of neighbouring molecules is ruled out as seen from the packing diagram (Fig. 2) and the

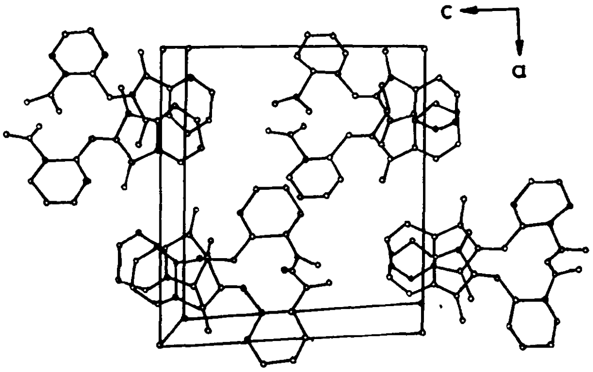

Fig. 2. The crystal packing.

intermolecular contact distances.* In this respect, the behaviour of the crystals of the title compound resembles that of the γ-modification of 2-*p*-dimethylaminobenzylidene-1,3-indandione (Magomeda, Zvonkova, Neigauz & Novakovskaya, 1980). In the α- and β-modifications, the intermolecular contacts are between dissimilar fragments leading to photosemiconductivity by electron charge transfer (Magmedova & Zvonkova, 1978, 1980).

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* See deposition footnote.

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Ethyl [3-(1,3-Dioxoindanylidene)-1-oxoindan-2-yl]acetate

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Abstract. $C_{22}H_{16}O_5$, $M_r = 360{\cdot}37$, monoclinic, $P2_1/n$, $a = 15{\cdot}857\ (5)$, $b = 6{\cdot}318\ (4)$, $c = 19{\cdot}667\ (5)$ Å, $\beta = 108{\cdot}89\ (2)°$, $V = 1864{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}284$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}54$ mm^{-1}, $F(000) = 752$, $T = 292$ K, $R = 0{\cdot}055$ for 2084 observed reflections. The C—O bond lengths in the ethoxycarbonylmethyl side chain indicate the presence of resonance structures of the carbonyl group. The molecule excluding the ethoxycarbonylmethyl side chain is essentially planar, while the side chain assumes an extended conformation.

Introduction. On account of the known biological activity of indan-1,3-dione and some of its derivatives, a number of structural studies of these compounds have been reported in recent years (*e.g.*, Csöregh & Eckstein, 1979, and references therein; Varghese, Srinivasan, Ramadas & Padmanabhan, 1986). The title compound is one of the new derivatives synthesized by Padmanabhan and Ramadas (Padmanabhan, 1982).

Experimental. Indan-1,3-dione on treatment with ethyl bromoacetate in the presence of freshly fused potassium carbonate in chloroform at room temperature gave a product containing two compounds. Column chromatography of this product on silica gel with benzene–hexane (2:1) furnished a new but unstable compound. The benzene eluates gave the stable title compound (m.p. 395 K). Recrystallization from ethanol gave shiny yellow needle-shaped crystals.

Crystal $0{\cdot}38 \times 0{\cdot}12 \times 0{\cdot}60$ mm, Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Cell parameters refined by least-squares method on the basis of 25 reflections ($2 < 2\theta < 30°$). Two check reflections did not show significant variation during data collection. Lp correction, no absorption correction, no extinctions. 3279 reflections having $I > 3\sigma(I)$, $2 < 2\theta < 30°$, $h \pm 16$, $k \pm 7$, $l \pm 8$. Structure solved by

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