Universidad de la República, Uruguay) and CONICYT (Consejo Nacional de Investigación Científica y Tecnológica, Uruguay) for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SX1003). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-(*p*-Diethylaminobenzylidene)-1,3-indandione

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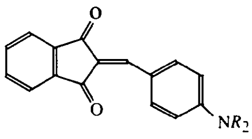
Abstract

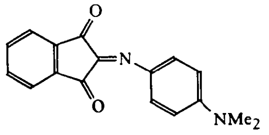
The title compound, $C_{20}H_{19}NO_2$, belongs to the class of donor–acceptor-substituted conjugated polyenes. Within the structure, O atoms are situated in the plane of the 1,3-indandione fragment and the N atom lies in the plane of the *p*-benzylidene fragment which forms a dihedral angle of 7.6 (2)° with the indandione nucleus.

Comment

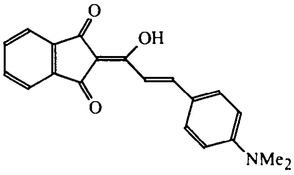
2-(*p*-Dimethylaminobenzylidene)-1,3-indandione, (I*b*), exhibits a series of unusual solid-state and solution photophysical properties, in particular non-linear optical behaviour and recently discovered non-linear fluorescent properties (Valkunas *et al.*, 1993, and references therein). When this derivative absorbs at 450–500 nm in solution, it forms three deeply coloured polymorphs: the most-stable dark-red α-modification (space group $P2_1/c$, $Z = 8$; Magomedova & Zvonkova, 1978), a less-stable blue-coloured β-modification (space group $P2_1/c$, $Z = 4$; Magomedova, Zvonkova, Neigaus & Novakovskaya, 1980), and the least-stable red prisms of the γ-modification (non-centrosymmetric space group $Pna2_1$, $Z = 4$; Magomedova & Zvonkova, 1980).



(I*a*) R = Et
(I*b*) R = Me



(II)



(III)

During our investigations on the synthesis and properties of structural analogues of (I*b*), we have found that the *p*-diethylamino derivative, the title compound (I*a*), always crystallizes as deep-green lustrous crystals, whereas its UV–visible absorption properties in solution (λ_{max} = 488 nm in dichloromethane) are practically the same as those of (I*b*). Solid-state investigations of this derivative may shed light on unusual polychromic properties of the whole series of electron-donor-substituted derivatives of 2-ylidene-1,3-indandiones.

The 1,3-indandione moiety of (I*a*) is planar [r.m.s. Δ = 0.012 (4) Å] and the two O atoms are displaced by 0.028 (5) (O1) and 0.059 (5) Å (O2) from the plane. The N atom is displaced from the plane of the *p*-phenyl ring [r.m.s. Δ = 0.003 (3) Å] by 0.12 (8) Å. The bond lengths within the bridge linking the 1,3-indandione accepting and diethylamino donating moieties exhibit the presence of considerable conjugation. Thus, the aromatic C12—C13 [1.376 (6) Å] and C15—C16 [1.373 (6) Å] bonds are slightly shorter than other aromatic bonds in the *p*-phenylene ring [1.396 (6)–1.400 (6) Å], indicating the *p*-quinoid character. All of the above-mentioned geometrical features are also typical of (I*b*), (II) [2-(4′-dimethylaminophenylimino)-1,3-indandione; Magomedova, Zvonkova, Geita, Novakovskaya, Neigaus & Belsky, 1980] and (III) [2-(4′-dimethylaminocinnamoyl)-1,3-indandione; Magomedova, Zvonkova, Geita, Smelyanskaya & Ginzburg, 1980].

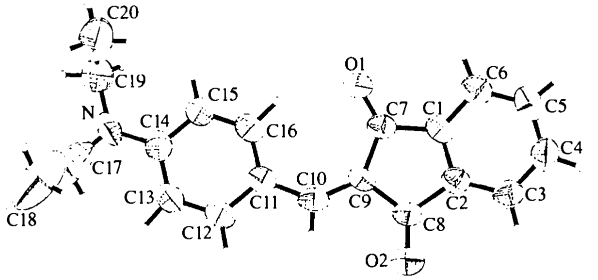


Fig. 1. Molecular structure of (I*a*) showing 50% probability displacement ellipsoids.

One of the interesting structural features of this group of compounds is the angle between the two planar donor and acceptor moieties in the molecule. The interplanar angles between the 1,3-indandione and *p*-phenyl moieties are 7.6 (2) in (I*a*), 0.3 and 7.8 in the two independent molecules of the α-modification of (I*b*), 3.5 in the β-modification of (I*b*), 7.4 in the γ-modification of (I*b*), 10.0 in (II) and 11.5° in (III). There seems to be no relationship therefore between the distortion from planarity of the molecules and their colour. The crystal packing of derivative (I*a*) differs from that of all three polymorphs of (I*b*). No notably short intermolecular contacts were observed in the crystal lattice of any of these derivatives. It is noteworthy that the blue-coloured β-modification of (I*b*) possesses the lowest calculated density, 1.31 g cm^{-3}, compared with the α-modification (1.332 g cm^{-3}) and γ-modification (1.331 g cm^{-3}). The calculated density for the title compound (I*a*) is only 1.251 g cm^{-3}.

Experimental

0.146 g (1 mmol) of 1,3-indandione and 0.177 g (1 mmol) of *p*-diethylaminobenzaldehyde were dissolved in 12 ml of hot acetic acid and three drops of concentrated HCl solution were added under stirring. The solution was refluxed for 5 min and then left to cool to room temperature for 1 h. 5 ml of water was added under stirring and the dark precipitate was filtered off and washed with hot water and methanol. The yield of crude (I*a*) was 0.28 g (92%). Opaque green crystals with metallic lustre (m.p. 427–428 K) were grown from acetonitrile.

Crystal data

$C_{20}H_{19}NO_2$
$M_r = 305.36$
Monoclinic
$P2_1/n$
$a = 7.611$ (3) Å
$b = 20.972$ (10) Å
$c = 10.312$ (4) Å
$\beta = 99.93°$
$V = 1621.3$ (12) Å^3
$Z = 4$
$D_x = 1.251$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 40 reflections
$\theta = 9$–25°
$\mu = 0.081$ mm^{-1}
$T = 293$ (2) K
Prism
0.40 × 0.37 × 0.21 mm
Deep green

Data collection

Syntex $P\bar{1}$ diffractometer
ω–2θ scans
Absorption correction: none
2316 measured reflections
2093 independent reflections
1337 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.1095$

$\theta_{\rm max} = 25.05°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 24$
$l = -12 \rightarrow 12$
2 standard reflections monitored every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0740$
$wR(F^2) = 0.2751$
$S = 1.033$
2018 reflections
208 parameters
H atoms riding with fixed $U_{\rm iso}$ for H atoms of methyl groups

$w = 1/[\sigma^2(F_o^2) + (0.1181P)^2 + 1.1272P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.007$
$\Delta\rho_{\rm max} = 0.401$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.448$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	$U_{\rm eq}$
O1	0.1686 (4)	0.4272 (2)	0.3401 (3)	0.0722 (10)
O2	−0.2787 (5)	0.5802 (2)	0.2002 (3)	0.0788 (11)
N	−0.2742 (6)	0.2747 (3)	0.7372 (5)	0.097 (2)
C1	0.1397 (6)	0.5142 (2)	0.1881 (4)	0.0495 (11)
C2	0.0103 (6)	0.5585 (2)	0.1437 (4)	0.0515 (11)
C3	0.0334 (7)	0.6033 (2)	0.0495 (5)	0.0630 (13)
C4	0.1912 (7)	0.6021 (2)	0.0009 (5)	0.0685 (14)
C5	0.3213 (7)	0.5585 (3)	0.0462 (5)	0.0692 (14)
C6	0.2985 (6)	0.5135 (2)	0.1405 (5)	0.0631 (13)
C7	0.0787 (6)	0.4713 (2)	0.2864 (4)	0.0496 (11)
C8	−0.1424 (6)	0.5481 (2)	0.2133 (4)	0.0541 (12)
C9	−0.0990 (6)	0.4923 (2)	0.3011 (4)	0.0468 (11)
C10	−0.2227 (6)	0.4710 (2)	0.3708 (4)	0.0538 (12)
C11	−0.2290 (6)	0.4196 (2)	0.4634 (4)	0.0511 (11)
C12	−0.3894 (6)	0.4089 (2)	0.5091 (5)	0.0622 (13)
C13	−0.4059 (7)	0.3612 (2)	0.5979 (5)	0.0694 (14)
C14	−0.2622 (7)	0.3216 (2)	0.6478 (5)	0.0672 (14)
C15	−0.1012 (6)	0.3323 (2)	0.6033 (4)	0.0601 (12)
C16	−0.0867 (6)	0.3796 (2)	0.5136 (4)	0.0576 (12)
C17	−0.4268 (9)	0.2756 (3)	0.8127 (7)	0.159 (4)
C18	−0.5598 (14)	0.2338 (3)	0.7340 (8)	0.184 (5)
C19	−0.1236 (8)	0.2322 (3)	0.7885 (6)	0.091 (2)
C20	−0.0910 (10)	0.1818 (3)	0.6961 (7)	0.110 (2)

Table 2. *Selected geometric parameters (Å, °)*

O1—C7	1.225 (5)	C11—C12	1.400 (6)
O2—C8	1.225 (5)	C12—C13	1.376 (6)
C9—C10	1.355 (6)	C13—C14	1.399 (7)
C10—C11	1.447 (6)	C14—C15	1.399 (6)
C11—C16	1.396 (6)	C15—C16	1.373 (6)
C9—C10—C11	134.5 (4)		

Restraints were applied to the C17—C18 and N—C17 bond lengths because of unresolved disorder in this ethyl group.

Data collection: *P*3 *Software* (Siemens, 1990). Cell refinement: *P*3 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

This work was supported in part by a grant from the Israeli Ministry of Science and Technology.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1092). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-(4-Nitrobenzyloximino)hexahydroazepin-2-one

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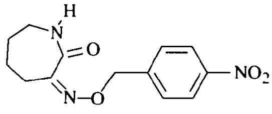
Abstract

The title compound, $C_{13}H_{15}N_3O_4$, occurs as two stereoisomers. The *Z* and *E* isomers both display potent relaxant activity. Crystal structure analysis clearly demonstrates that the studied isomer, the less active form, adopts the *Z* conformation. The molecules are held together by N—H···O hydrogen bonds and intermolecular ring-to-ring interactions forming head-to-tail hydrogen-bonded dimers and a layered π-stacking arrangement.

Comment

This work is part of a general program aiming to synthesize new potential relaxant molecules. One derivative of the oximinocaprolactame family, 3-[*O*-(4-nitrobenzyl)oximino ether]hexahydroazepine-2-one (NOHA), displays promising anti-convulsive activity (Elfrom, 1995) of almost the same order as that of the reference relaxant agents theophilline and cromakalim. Cross-reference tests on NOHA showed that its activity depends strongly on the nature and/or the position of the different functional groups of the molecule. Thus, changing the position of NO_2 on the phenyl group in NOHA or substitution of the caprolactame, a seven-membered heterocycle (C_6NO), by a benzene ring seriously affects its activity.



Z-NOHA

Thin-layer chromatography and NMR studies showed that two stereoisomers, the *Z* and *E* forms, coexist in NOHA. Subsequent pharmacological tests showed that the *E* isomer is 1.5 times more active than the *Z* form. For structure–activity-correlation purposes, the geometrical properties of both isomers are of interest. Unfortunately, only single crystals of *Z* are available as efforts to grow the *E* isomers have so far been unsuccessful. However, it was decided to perform a crystal structure determination of the *Z* isomer with the assumption that the molecular structures of both isomers should be similar; the molecular geometry of the *Z* form could also be helpful in solving the structure of the *E* isomer by powder methods. The crystal structure solution confirms the *Z* conformation of the title compound. The molecules are packed in an extensive benzene–benzene π-stacking arrangement (ring–ring distance 3.4 Å) and as head-to-tail hydrogen-bonded dimers [N3···O4($1-x$, $-y$, $1-z$) = 2.977 (6) Å].

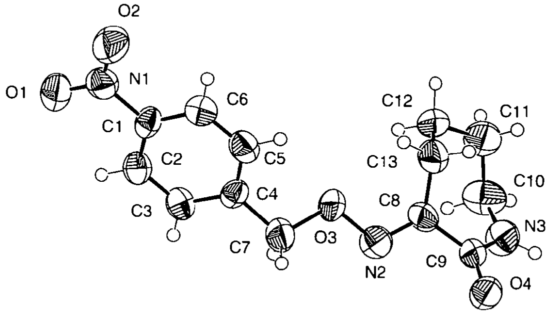


Fig. 1. The molecular structure of Z-NOHA showing the atom-labelling scheme with 50% probability displacement ellipsoids.