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Structure of 3-Benzoyl-4-methyl-1-phenyl-1,2,3,4-tetrahydro-5*H*-indeno-[1,2-*b*]pyridine-2,5-dione

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Abstract. $C_{26}H_{19}NO_3$, $M_r = 393.442$, triclinic, $P\bar{1}$, $a = 8.630$ (1), $b = 9.908$ (4), $c = 13.549$ (16) Å, $\alpha = 107.73$ (3), $\beta = 94.96$ (5), $\gamma = 112.51$ (3)°, $V = 991.85$ (1.31) Å^3, $Z = 2$, $D_m = 1.30$, $D_x = 1.317$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.080$ mm^{-1}, $F(000) = 412$, $T = 293$ K, $R = 0.050$ for 2110 unique observed reflections. The pyridone ring has a half-chair conformation with in-ring torsions in the N—C(carbonyl) and N—C(indenyl) bonds of 6.3 (5) and 15.6 (5)°, respectively. The phenyl-substituted N is planar to within 0.013 (3) Å.

Introduction. Both 5*H*- and 1*H*-indeno[1,2-*b*]pyridine derivatives have a wide spectrum of biological activity, *e.g.* antidepressant (Leven & Schacht, 1984), antihistaminic (Vinogradova, Gaivoronskaya, Kirillova, Bu Habib & Prostakov, 1984), plant-growth regulatory (Wieczorek, Boduszek, Gancarz & Zukiewicz, 1984), and are present in many alkaloids (Koyama, Sugita, Suzuta & Irie, 1979; Waterman & Muhammad, 1985; Goulart, Sant'ana, De Oliveira, De Oliveira & Maia, 1986; Wu, 1989; Bon-Abdullah, Jossang, Tadic, Lebceuf & Cave, 1989). In a study of the reaction of methylene-bis-anilides of benzoylacetic derivatives with excess phosphorus oxychloride,

elemental and spectral analysis as well as isotopic and chemical evicence suggested that 2*H*-pyrano[2,3-*b*]quinolin-2-one was the reaction product (Zankowska-Jasińska & Kolasa, 1976). Because this relatively simple and very efficient synthesis should lead, according to our assumption, to a common constituent of alkaloid structures we decided to choose a stereochemically interesting derivative for X-ray investigation. Much to our surprise the result revised the previously postulated structure of the reaction product of 2,4-dibenzoyl-3-methyl-pentanedioic acid dianilide with POCl$_3$ and thus revealed indirectly the course of the reaction, *i.e.* that aniline and not water is eliminated first.

Experimental. The compound crystallizes from methanol at room temperature as orange prisms. A crystal 0.2 × 0.1 × 0.05 mm was chosen. X-ray measurements were made using an Enraf–Nonius FAST area detector and graphite-monochromated Mo $K\alpha$ radiation from a rotating-anode generator operating at 47 kV, 47 mA with a 300 μm focus. With a detector-to-crystal setting (=DET) of 40 mm and a swing angle (=θ_D) of −18°, reflections were found in two 5° ω-rotation regions separated by 90°.

Orientation matrix and unit-cell dimensions were determined via the *INDEX* and *REFINE* procedures of the *SADONL* software [the 'small molecule' online version of MADNES (1991)] using 50 reflections taken from both regions. Accurate values of DET (40.325) and θ_D $(-17.951°)$ were also determined, along with improved cell dimensions, by refinement using 250 reflections with $\theta \leq 27°$ from the two regions. The refined mosaic spread was 0.634°. Unit-cell refinement was subsequently performed at ω-rotation intervals of 15° during data collection. Intensity data corresponding to slightly more than one hemisphere of reciprocal space were recorded using two ω-scan ranges of 100° with a φ shift of 90° (to achieve $> 180°$ in total) at $\chi = \theta°$, followed by two ω rotations of 70°, with a φ shift of 90° at $\chi = 90°$, to record the missing cusp data. Throughout the data collection the ω increment for each frame was 0.10° and measuring time 20 s; the total data collection time was *ca* 18 h. The total of 5943 reflections which satisfied the conditions for acceptable measurement were merged to give 3057 unique data, with $R_{merge} = 0.055$. Reflections with $F < 4\sigma(F)$ were considered unobserved. A $\sin\theta$ limit of 0.4067 (to ensure a spherical data set and thus no possible bias in scaling for direct methods and refinement) reduced the number of observed reflections to 2110. Data processing included corrections for Lp effects and area detector specific factors. No correction for absorption was made. The structure was solved by automatic centrosymmetric direct methods using *SHELXS*86 (Sheldrick, 1986) and refined in $P\bar{1}$ with *SHELX*80 (Sheldrick, 1980) employing full-matrix least squares on F_o. All non-H

atoms were refined anisotropically and H atoms isotropically together with their positions found from the difference Fourier map for all but one of the methyl-group H atoms, which was geometrically positioned. The total number of refined parameters was 347 and comprised 270 for non-H atoms and 76 for H atoms. Four reflections (111, 010, 100, 046) suffering from extinction were omitted in the last cycles of refinement. The weights used were $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$. Refinement was terminated at $R = 0.050$, $wR = 0.060$ with $g = 0.0009$; final electron density $\Delta\rho(max.) = 0.177$, $\Delta\rho(min.) = -0.214$ e Å^{-3}, max. shift/e.s.d. for temperature factor of H(12) in final least-squares cycle was 0.2. Geometrical calculations were performed with the *PARST* program (Nardelli, 1983).

Discussion. The molecular structure of the title compound, together with the atom-numbering scheme, is shown in Fig. 2. It is composed of two structural units: 5*H*-indeno[1,2-*b*]pyridine and benzoyl. The atomic parameters are listed in Table 1.* The bond lengths and angles, selected torsion angles, and puckering and the lowest asymmetry parameters (as defined by Nardelli, 1983) for 2-pyridone and the cyclopentadienone ring are given in Table 2. The analysis of the bonds of the amide moiety shows the typical C=O double-bond length of 1.206 (4) Å and nearly equal bonds between the planar, and thus sp^2, N atom and the two neighbouring sp^2 C atoms, C(2) and C(13). This suggests that any interaction between the lone pair of the N(1) atom and the π

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54935 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0079]
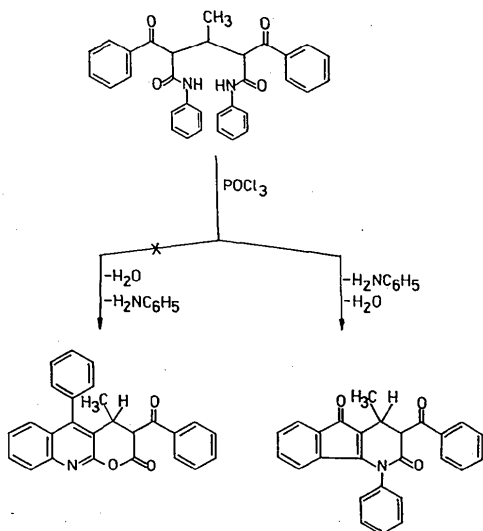

Fig. 1. Scheme of cyclization of 2,4-dibenzoyl-3-methyl-pentanedioic acid dianilide in the presence of POCl₃ showing the importance of the aniline and water splitting sequence.
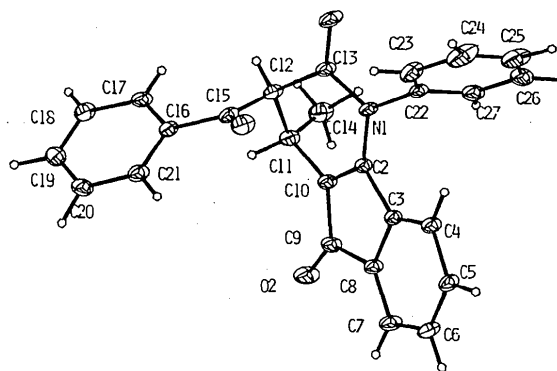

Fig. 2. The molecule with atom-numbering scheme. Thermal vibration ellipsoids are scaled to enclose 20% probability. The program used was *SNOOPI*, written by Dr E. K. Davies, Chemical Crystallography Laboratory, Oxford, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^4$) *with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}
O(1)	3297 (3)	7115 (2)	1681 (2)	687 (6)
O(2)	-2065 (3)	10101 (2)	1622 (1)	599 (6)
O(3)	3937 (3)	10797 (2)	3099 (1)	641 (6)
N(1)	1134 (3)	7444 (2)	2402 (2)	443 (7)
C(2)	6 (3)	8132 (3)	2456 (2)	396 (6)
C(3)	-1024 (3)	8297 (3)	3275 (2)	394 (7)
C(4)	-1149 (3)	7889 (3)	4162 (2)	455 (8)
C(5)	-2184 (3)	8316 (3)	4806 (2)	499 (8)
C(6)	-3055 (3)	9123 (3)	4576 (2)	549 (7)
C(7)	-2941 (3)	9530 (3)	3680 (2)	514 (7)
C(8)	-1922 (3)	9111 (3)	3044 (2)	404 (7)
C(9)	-1485 (3)	9441 (3)	2064 (2)	437 (7)
C(10)	-253 (3)	8810 (3)	1775 (2)	416 (7)
C(11)	685 (3)	8870 (3)	898 (2)	482 (7)
C(12)	2475 (4)	9004 (3)	1330 (2)	475 (7)
C(13)	2358 (4)	7763 (3)	1798 (2)	493 (8)
C(14)	-280 (4)	7444 (4)	-125 (2)	715 (8)
C(15)	3592 (3)	10625 (3)	2171 (2)	462 (7)
C(16)	4170 (3)	11992 (3)	1829 (2)	437 (6)
C(17)	4470 (4)	11883 (3)	829 (2)	514 (6)
C(18)	5080 (4)	13201 (3)	565 (2)	598 (8)
C(19)	5299 (4)	14619 (3)	1279 (2)	605 (8)
C(20)	4971 (4)	14745 (3)	2269 (2)	634 (7)
C(21)	4428 (4)	13442 (3)	2550 (2)	543 (8)
C(22)	1006 (3)	6332 (3)	2898 (2)	435 (7)
C(23)	2305 (4)	6668 (4)	3714 (2)	650 (8)
C(24)	2105 (5)	5550 (5)	4184 (3)	936 (9)
C(25)	642 (6)	4188 (4)	3833 (3)	1005 (8)
C(26)	-636 (5)	3870 (3)	3026 (3)	823 (8)
C(27)	-448 (4)	4941 (3)	2557 (2)	598 (8)

Table 2. *Selected geometric parameters* (Å, °), *with e.s.d.'s in parentheses*

C(3)—C(2)	1.490 (4)	C(3)—C(8)	1.392 (4)
C(4)—C(3)	1.380 (4)	C(4)—C(5)	1.393 (5)
C(6)—C(5)	1.368 (5)	C(6)—C(7)	1.390 (5)
C(7)—C(8)	1.371 (5)	C(9)—C(8)	1.506 (5)
C(9)—C(10)	1.451 (5)	C(10)—C(2)	1.345 (4)
C(10)—C(11)	1.498 (4)	C(2)—N(1)	1.381 (4)
C(13)—N(1)	1.392 (4)	C(11)—C(12)	1.545 (6)
C(12)—C(13)	1.521 (5)	C(12)—C(15)	1.522 (6)
C(15)—C(16)	1.485 (4)	C(22)—N(1)	1.431 (4)
C(13)—O(1)	1.206 (4)	C(9)—O(2)	1.216 (4)
C(15)—O(3)	1.211 (4)		
C(16)—C(21)	1.389 (5)	C(22)—C(27)	1.369 (5)
C(16)—C(17)	1.380 (4)	C(22)—C(23)	1.366 (5)
C(17)—C(18)	1.380 (5)	C(23)—C(24)	1.402 (5)
C(18)—C(19)	1.372 (5)	C(24)—C(25)	1.357 (6)
C(29)—C(20)	1.374 (5)	C(25)—C(26)	1.351 (6)
C(20)—C(21)	1.377 (5)	C(26)—C(27)	1.362 (5)
C(22)—N(1)—C(2)	121.5 (3)	C(13)—N(1)—C(2)	119.3 (3)
C(10)—C(2)—N(1)	123.2 (3)	C(10)—C(2)—C(3)	110.5 (3)
C(27)—C(22)—N(1)	119.1 (3)	C(23)—C(22)—N(1)	120.3 (3)
C(17)—C(16)—C(15)	122.7 (3)	C(21)—C(16)—C(15)	118.4 (3)
C(16)—C(15)—O(3)	121.1 (3)	C(12)—C(15)—O(3)	120.6 (3)
C(12)—C(15)—C(16)	118.2 (3)	C(6)—C(5)—C(4)	121.4 (3)
N(1)—C(13)—O(1)	121.2 (3)	C(12)—C(13)—O(1)	122.4 (3)
C(12)—C(13)—N(1)	116.3 (3)	C(3)—C(8)—C(9)	107.9 (3)
C(7)—C(8)—C(9)	130.4 (2)	C(7)—C(8)—C(3)	121.7 (3)
C(8)—C(9)—O(2)	126.0 (3)	C(10)—C(9)—O(2)	128.2 (3)
C(10)—C(9)—C(8)	105.9 (3)	C(13)—C(12)—C(15)	109.2 (3)
C(11)—C(12)—C(15)	110.8 (3)	C(11)—C(12)—C(13)	112.5 (3)
C(8)—C(3)—C(2)	106.5 (3)	C(4)—C(3)—C(2)	133.3 (2)
C(4)—C(3)—C(8)	120.0 (3)	C(6)—C(7)—C(8)	118.1 (3)
C(9)—C(10)—C(2)	109.1 (3)	C(11)—C(10)—C(2)	121.6 (3)
C(11)—C(10)—C(9)	129.3 (3)	C(10)—C(11)—C(12)	106.1 (3)
C(14)—C(11)—C(12)	111.7 (3)	C(14)—C(11)—C(10)	112.5 (3)
C(7)—C(6)—C(5)	120.7 (4)	C(3)—C(4)—C(5)	118.2 (3)
C(3)—C(8)—C(9)—C(10)	-1.7 (4)	C(2)—C(10)—C(11)—C(12)	-32.7 (4)
C(8)—C(9)—C(10)—C(2)	1.8 (4)	C(10)—C(11)—C(12)—C(13)	50.8 (4)
C(9)—C(10)—C(2)—C(3)	-1.3 (4)	C(11)—C(12)—C(13)—N(1)	-40.7 (4)
C(10)—C(2)—C(3)—C(8)	0.2 (4)	C(12)—C(13)—N(1)—C(2)	6.3 (5)
C(2)—C(3)—C(8)—C(9)	0.9 (3)	C(13)—N(1)—C(2)—C(10)	15.6 (5)
O(1)—C(13)—N(1)—C(22)	0.5 (5)	C(9)—C(10)—C(2)—C(3)	-1.3 (4)

Puckering and lowest asymmetry parameters

Cyclopentadienone ring	2-Pyridone ring
$q_2 = 0.017$ (3) Å, $\varphi_2 = 112.8$ (12.3)°	$q_2 = 0.411$ (3) Å, $q_3 = -0.210$ (1) Å
$\Delta C_s[C(9)] = 0.001$ (2)	$\varphi_2 = -24.33$ (4)°
	$Q = 0.462$ (3) Å, $\theta_2 = 117.1$ (4)°
	$\Delta C_2[C(2)—N(1)] = 0.026$ (1)

systems C(13)=O(1) and C(2)=C(10) is equally distributed. Values of torsion angles in the 2-pyridone ring, especially C(2)—C(10)—C(11)—C(12), C(10)—C(11)—C(12)—C(13) and C(11)—C(12)—C(13)—N(1), show the ring to be decidedly non-planar. It has a half-chair conformation with a pseudo-diad axis intersecting the N(1)—C(2) and C(11)—C(12) bonds. It is also to be noted that the in-ring torsion angles about C(13)—N(1) and N(1)—C(2), potential sites for delocalization of the N(1) lone pair, are 6.3 (5) and 15.6 (5)°, indicating that those systems are not completely planar. On the other hand, the torsion angles involving external substituents, O(1)— C(13)—N(1)—C(22) and C(9)—C(10)—C(2)—C(3), are very close to 0. The cyclopentadienone ring shows a small deviation from an envelope conformation with a very small asymmetry parameter corresponding to a pseudo mirror plane through C(9). Cyclopentadienone is nearly coplanar with the benzene ring. The molecule has two asymmetric C atoms C(11) and C(12), but the space group is centrosymmetric and the crystals are racemic. The molecule whose coordinates are given in Table 1 is *R* at C(11) and *S* at C(12).

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Structure of 4-Bromopyrazabole

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Abstract. $C_6H_9B_2BrN_4$, $M_r = 238.7$, monoclinic, $P2_1/n$, $a = 6.756$ (2), $b = 13.012$ (4), $c = 10.931$ (4) Å, $\beta = 91.50$ (2)°, $V = 960.6$ (5) Å^3, $Z = 4$, $D_x = 1.650$ Mg m^{-3}, Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu = 5.510$ mm^{-1}, $F(000) = 472$, $T = 108$ (2) K, $R = 4.45\%$, 1185 unique observed data. The molecule has a butterfly arrangement of three condensed rings with a boat-shaped central B_2N_4 moiety. The Br is bonded to the B in an axial position with a B—Br length of 2.075 (5) Å. The shorter B—N bond distances in the N_2BHBr group [1.530 (6) Å ave.] compared to the B—N bonds in the N_2BH_2 group [1.562 (7) Å ave.] suggest that the N_2BHBr group is the stronger Lewis acid.

Introduction. The synthesis of pyrazabole and a few of its derivatives was first reported by Trofimenko (1966). Since then, dozens of other pyrazaboles have been reported; this subject was recently reviewed by Niedenzu (1988). The compound 4-bromopyrazabole was found to be thermally unstable with respect to formation of 4,8-dibromopyrazabole and pyrazabole (Hanecker, Hodgkins, Niedenzu & Nöth, 1985). A study of the crystal structure of 4-bromopyrazabole was undertaken to look for structural reasons for this instability.

Experimental. A sample of 4-bromopyrazabole was synthesized from boron tribromide and a molar excess of pyrazabole according to Hanecker, Hodgkins, Niedenzu & Nöth (1985). Unreacted pyrazabole was removed by sublimation over a three day period at bath temperatures of 312–316 K. A small portion of the white powdery residue was then placed in an ampoule, and the ampoule was sealed under vacuum. The bottom 1 cm of this ampoule was heated in a mineral bath at bath temperatures of 313–318 K; the rest of the ampoule was cooled to ambient temperature by a stream of air. During the next 22 d, colorless prismatic crystals were slowly deposited on the inside surface of the ampoule just above the level of the mineral oil.

A colorless prism of dimensions $0.20 \times 0.25 \times 0.45$ mm was mounted on a Syntex *P*1 diffractometer equipped with a nitrogen gas-stream sample cooler. Cell parameters were determined from the setting angles of 24 intensity maxima with 2θ values from 41 to 50°. Intensity data were measured using ω scans with a scan range of 0.40° and a variable scan speed of 2 to 12° min^{-1}. Stationary crystal/stationary counter background measurements were made 0.8° ω above and below peak maxima for 16.7% of the total scan time. A semi-empirical absorption correction was applied to the data giving minimum and maximum transmission factors of 0.007 and 0.743. Intensity data were collected in the 2θ range 3.5 to 114° with $-7 \le h \le 2$, $0 \le k \le 14$, $-11 \le l \le 11$. Three standard peaks ($\bar{3}1\bar{3}$, $\bar{2}5\bar{1}$, 035) were remeasured every 50 data with a maximum variation of 0.02. The 1949 measured data were merged giving 1293 unique data with $R_{int} = 6.49\%$. The structure was solved by direct methods. The structure was refined by full-matrix least squares on F using 1185 observed $[F > 4\sigma(F)]$ data. Initial positions of H