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Structure of Ethyl 5-Methoxy-3-phenyl-2-indolecarboxylate

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Abstract. $C_{18}H_{17}NO_3$, $M_r = 295{\cdot}34$, monoclinic, $C2/c$, $a = 11{\cdot}689\ (2)$, $b = 22{\cdot}934\ (4)$, $c = 11{\cdot}592\ (2)$ Å, $\beta = 100{\cdot}16\ (3)°$, $V = 3058{\cdot}8\ (8)$ Å^3, $Z = 8$, $D_m = 1{\cdot}30\ (5)$, $D_x = 1{\cdot}28$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ(Mo $K\alpha$) = 0·094 mm^{-1}, $F(000) = 1248$, $T = 300$ K, final $R = 0{\cdot}046$ for 1849 observed reflections [$I > 3\sigma(I)$]. The indole nucleus is slightly bent along the C(8)—C(9) bond. The phenyl ring connected to the indole moiety is rotated about the C(3)—C(10) bond by 45·8 (3)°. The carboxyl group makes a dihedral angle of 8·1 (4)° with the mean plane of the indole moiety. Centrosymmetrically related pairs of molecules are linked through hydrogen bonds across the centre of symmetry and form dimers.

Introduction. Indole derivatives possess important pharmacological properties, for example, as anti-allergic, CNS depressant and muscle relaxant agents (Harris & Uhle, 1960; Wei & Stanley, 1970; Reynolds & Carson, 1970; Ho, Haegman & Perisco, 1986). The title compound having a —$COOC_2H_5$ group next to the indole N atom serves as a versatile starting material to synthesize fused indole heterocycles of biological importance. The study of the title compound was undertaken because very little crystallographic information is available on non-steroidal indole derivatives (Chakraborthy & Talapatra, 1986). This work is part of our investigations on some pharmacologically important indoles and their precursors. The compound was synthesized by Fisher indolization (Huges, Lions, McKean, Murry, Callanan, Freeman, Ralph, Rossack, Dornbroski, Finch, Andrews, Betty, Scott, Vernon, Flack & Lawrence, 1938) of ethyl pyruvate *p*-methoxyphenylhydrazone using dry HCl gas.

Experimental. Needle-shaped pale-yellow crystals grown by diffusion of hexane into benzene solution. Crystal of size 0·2 × 0·15 × 0·15 mm mounted on an Enraf–Nonius CAD-4 diffractometer, $\omega/2\theta$ scan, max. time spent on any reflection 60 s. Cell dimensions from least-squares refinement of 25 centred reflections in the θ range 10–25°. Density by flotation technique. Intensity data collected using Mo $K\alpha$ radiation to $2\theta_{\max} = 60°$, 2927 independent reflections, $0 \le h \le 13$, $0 \le k \le 25$, $-13 \le l \le 13$, 1849 reflections with $I \ge 3\sigma(I)$ considered observed, data corrected for Lorentz–polarization effects, no absorption correction. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All H atoms located from successive difference Fourier maps, full-matrix least-squares refinement on F with anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms using *SHELX*76 (Sheldrick, 1976). The final $R = 0{\cdot}046$ and $wR = 0{\cdot}058$, $w = [\sigma^2(F) + 0{\cdot}02695F^2]^{-1}$, σ's based on counting statistics, the refinement terminated when the shift/e.s.d. in the positional parameters of non-H atoms was less than 0·02. 267 parameters were refined. The min. and max. electron densities in the final difference Fourier map were −0·29 and 0·23 e Å^{-3}. The scattering factors for C, N, O and H are those incorporated in *SHELX*76 (Sheldrick, 1976).

Discussion. The final positional parameters of non-H atoms with $U_{\rm eq}$ values are given in Table 1* and the bond lengths and angles are given in Table 2. An *ORTEP* (Johnson, 1965) plot of the molecule with 50% probability thermal ellipsoids with atomic numbering is shown in Fig. 1.

The two rings in the indole ring system are planar and the two rings are inclined to each other along the C(8)—C(9) bond. The normals to these planes are inclined at an angle of 1·7 (4)° and this appears to be statistically significant from zero (Falkenberg & Carlstrom, 1971). The methoxy group at C(5) is

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54062 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^4) *for non*-H *atoms with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}
N(1)	8891 (2)	−57 (1)	1320 (2)	437 (7)
C(2)	8678 (2)	522 (1)	1470 (2)	398 (7)
C(3)	7904 (2)	587 (1)	2243 (2)	385 (7)
C(4)	6871 (2)	−218 (1)	3281 (2)	425 (8)
C(5)	6809 (2)	−813 (1)	3398 (2)	491 (8)
C(6)	7476 (3)	−1190 (1)	2821 (3)	555 (10)
C(7)	8204 (2)	−982 (1)	2116 (2)	513 (9)
C(8)	8275 (2)	−382 (1)	1982 (2)	413 (7)
C(9)	7634 (2)	6 (1)	2569 (2)	404 (7)
C(10)	7424 (2)	1123 (1)	2688 (2)	354 (7)
C(11)	7378 (2)	1174 (1)	3875 (2)	416 (8)
C(12)	6954 (2)	1678 (1)	4320 (2)	490 (8)
C(13)	6564 (2)	2134 (1)	3584 (3)	542 (9)
C(14)	6586 (2)	2084 (1)	2399 (3)	535 (9)
C(15)	6995 (2)	1587 (1)	1946 (2)	450 (7)
O(16)	6107 (2)	−1095 (1)	4061 (2)	648 (7)
C(17)	5376 (3)	−741 (2)	4622 (3)	669 (12)
C(18)	9323 (2)	931 (1)	843 (2)	394 (7)
O(19)	9908 (2)	777 (1)	134 (2)	557 (4)
O(20)	9205 (2)	1481 (1)	1139 (2)	551 (6)
C(21)	9813 (3)	1918 (1)	580 (4)	696 (13)
C(22)	9355 (4)	2494 (1)	790 (4)	780 (15)

Table 2. *Bond lengths* (Å) *and angles* (°) *for molecules A and B with e.s.d.'s in parentheses*

N(1)—C(2)	1·368 (3)	C(8)—C(9)	1·412 (3)
N(1)—C(8)	1·364 (3)	C(10)—C(11)	1·392 (3)
C(2)—C(3)	1·389 (3)	C(10)—C(15)	1·404 (3)
C(2)—C(18)	1·474 (3)	C(11)—C(12)	1·392 (3)
C(3)—C(9)	1·436 (3)	C(12)—C(13)	1·376 (4)
C(3)—C(10)	1·481 (3)	C(13)—C(14)	1·382 (4)
C(4)—C(5)	1·375 (4)	C(14)—C(15)	1·377 (4)
C(4)—C(9)	1·414 (3)	O(16)—C(17)	1·417 (4)
C(5)—C(6)	1·410 (4)	C(18)—O(19)	1·211 (3)
C(5)—O(16)	1·380 (3)	C(18)—O(20)	1·321 (3)
C(6)—C(7)	1·365 (4)	O(20)—C(21)	1·445 (3)
C(7)—C(8)	1·388 (4)	C(21)—C(22)	1·462 (4)

C(2)—N(1)—C(8)	109·4 (2)	C(3)—C(9)—C(8)	107·3 (2)
N(1)—C(2)—C(3)	109·9 (2)	C(4)—C(9)—C(8)	119·7 (2)
N(1)—C(2)—C(18)	115·8 (2)	C(3)—C(10)—C(11)	119·8 (2)
C(3)—C(2)—C(18)	134·2 (2)	C(3)—C(10)—C(15)	122·2 (2)
C(2)—C(3)—C(9)	105·6 (2)	C(11)—C(10)—C(15)	118·0 (2)
C(2)—C(3)—C(10)	130·1 (2)	C(10)—C(11)—C(12)	121·0 (2)
C(9)—C(3)—C(10)	124·4 (2)	C(11)—C(12)—C(13)	120·1 (2)
C(5)—C(4)—C(9)	117·9 (2)	C(12)—C(13)—C(14)	119·4 (2)
C(4)—C(5)—C(6)	121·3 (2)	C(13)—C(14)—C(15)	121·1 (2)
C(4)—C(5)—O(16)	124·6 (2)	C(14)—C(15)—C(10)	120·4 (2)
C(6)—C(5)—O(16)	114·2 (2)	C(5)—O(16)—C(17)	116·9 (2)
C(5)—C(6)—C(7)	121·6 (2)	C(2)—C(18)—O(19)	123·2 (2)
C(6)—C(7)—C(8)	118·0 (2)	C(2)—C(18)—O(20)	113·3 (2)
N(1)—C(8)—C(7)	130·7 (2)	O(19)—C(18)—O(20)	123·5 (2)
N(1)—C(8)—C(9)	107·8 (2)	C(18)—O(20)—C(21)	117·6 (2)
C(7)—C(8)—C(9)	121·5 (2)	O(20)—C(21)—C(22)	109·1 (3)
C(3)—C(9)—C(4)	133·0 (2)		

coplanar with the indole system. The angle C(4)—C(5)—O(16) is larger than the C(6)—C(5)—O(16) angle by about 10° and this might be due to the *cis* orientation of C(4)—C(5) and O(16)—C(17) about C(5)—O(16) bond causing repulsion between C(4) and C(17) (Sakaki, Sogo, Wakahara, Kanai, Fujiwara & Tomita, 1976). The phenyl ring attached to C(3) is planar and the bond lengths and angles are normal. The mean plane through the phenyl ring makes a dihedral angle of 45·8 (3)° with the mean plane of the indole system. The bond lengths and angles in the ethoxycarbonyl group agree with the reported values. The apparent decrease in the bond lengths of the ethyl group as compared to the standard C_{sp^3}—C_{sp^3} bond distance might be due to the strong thermal vibrations of the terminal C atoms. The mean plane through the ethoxycarbonyl group is inclined to the mean plane of the indole rings at an angle of 8·1 (4)°.

The projection of the unit cell down **a** is shown in Fig. 2 and the stereoview of the packing down **a** is shown in Fig. 3. The centrosymmetrically related molecules are linked through N—H···O hydrogen bonds across the centre of symmetry and form dimers [H(1)···O(19)′ = 2·126, N(1)···O(19)′ = 2·893 (3) Å, angle N(1)—H(1)···O(19)′ = 158 (3)°]. In addition there are a few short contacts separated by distances less than 3·4 Å.

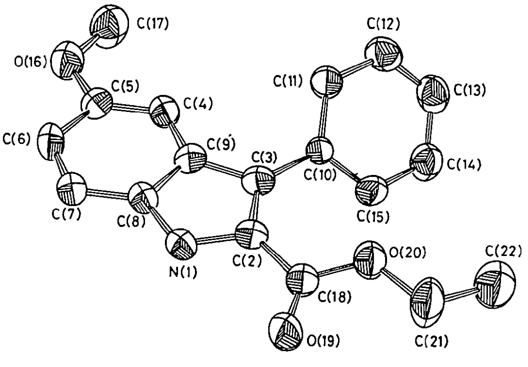

Fig. 1. *ORTEP* (Johnson, 1965) plot of the molecule with 50% probability thermal ellipsoids with atomic numbering.

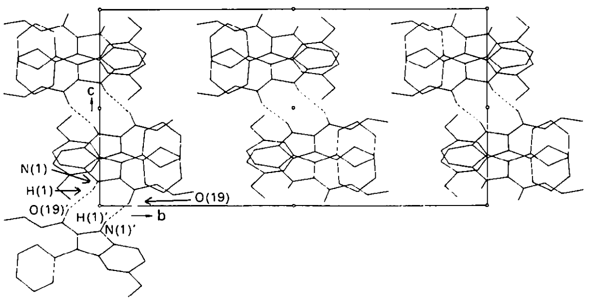

Fig. 2. Projection of the unit cell down **a**, broken lines indicate hydrogen bonds.

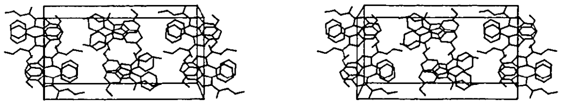

Fig. 3. Stereoview of the packing down **a**.

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Structure of the Organic Conductor $(BEDT\text{-}TTF)_2Br.C_2H_4(OH)_2$

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Abstract. Bis[3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalenium] bromide–ethylene glycol (1/1), $2C_{10}H_8S_8^{1/2+}.Br^-.C_2H_6O_2$, $M_r = 911.3$, monoclinic, $P12_1/n1$, $a = 14.950\ (2)$, $b = 33.692\ (4)$, $c = 6.621\ (1)$ Å, $\beta = 92.44\ (1)°$, $V = 3331.8\ (8)$ Å^3, $Z = 4$, $D_x = 1.82$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1.541$ Å, $\mu = 107.1$ cm^{-1}, $R = 0.071$ for a total of 3115 independent reflections. The title compound is a new organic conductor [$\sigma(300) = 8\ \Omega^{-1}$ cm^{-1}, with a metal–insulator transition at $T = 196$ K]. The structure is laminated. Cation and anion layers are parallel to the *ac* plane and alternate along the *b* axis. BEDT-TTF cations form stacks along the *a* axis. The anion layers consist of Br^- ions and ethylene glycol molecules linked by hydrogen bonds, Br···H—O. In the cation layer, BEDT-TTF ions from neighbouring stacks are linked, in side-by-side bands, by short intermolecular contacts S···S 3.448 (4)–3.508 (4) Å. No short S···S contacts were found in the stacks.

Introduction. At present there are more than 40 organic superconductors known (Ishiguro, 1988). The cation-radical salts based on bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF), which become superconducting at low temperature and at ambient pressure or under high pressure, constitute a considerable part of them and have a typical cation–anion ratio, *C*:*A* of 2:1. Scarce data on the structure and properties of the BEDT-TTF salts with monoatomic anions: $(BEDT\text{-}TTF)_3Br_2.(H_2O)_2$ (Urayama, Saito, Kawamoto & Tanaka, 1987), $(BEDT\text{-}TTF)_3Cl_2.(H_2O)_2$ (Mori & Inokuchi, 1987*a*,*b*; Rosseinsky, Kurmoo, Talham, Day, Chasseau & Watkin, 1988) and β-$(BEDT\text{-}TTF)_3Br_2$ (Parkin, Engler, Lee & Schumaker, 1985) testify to the fact that these compounds have a *C*:*A* ratio of 3:2 and a metal–insulator transition temperature (T_{MI}) of 100–185 K. An exception is the salt $(BEDT\text{-}TTF)_3Cl_2.(H_2O)_2$ which is a superconductor at $T_c = 2$ K and pressure of $P_c = 16$ kbar (Mori & Inokuchi, 1987*a*,*b*). It has been shown (Shibaeva, Lobkovskaya, Rozenberg, Buravov, Ignatiev, Kushch, Laukhina, Makova, Yagubskii & Zvarykina, 1988) that changing the *C*:*A* ratio to 2:1 in the $(BEDT\text{-}TTF)_4Cl_2.4H_2O$ salt brings T_{MI} down to 20 K. In order to obtain compounds with monohaloid anions

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