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Structure of N,N-Bis(o-nitrobenzyl)tryptamine

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Abstract. 3-[2-Bis(2-nitrobenzyl)aminoethyl]-1*H*-indole, $C_{24}H_{22}N_4O_4$, $M_r = 430.46$, monoclinic, $P2_1$, $a = 7.689$ (1), $b = 14.041$ (1), $c = 10.438$ (1) Å, $\beta = 106.25$ (7)°, $V = 1081.9$ (4) Å^3, $Z = 2$, $D_x = 1.321$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1.54184$ Å, $\mu = 7.16$ cm^{-1}, $F(000) = 452$, $T = 291$ K, final $R = 0.0457$ for 1958 reflections and 333 parameters. The two nitrobenzyl substituents differ in conformational and thermal properties. Both nitro groups participate in an inter-molecular bifurcated hydrogen bond. The geometry of the indole ring system is in agreement with previous investigations of indole amines.

Introduction. As part of a study of organic synthesis routes to quinazolinocarboline alkaloids (Bergman & Bergman, 1985), a group of naturally occurring and biologically active substances, the structure of the title reaction intermediate was established by X-ray analysis. Tryptamine derivatives can be found in mammals as well as in plants, and their biological effects on the central nervous system have been the cause of many investigations. In connection with these, several structural studies have been undertaken (Falkenberg & Carlström, 1971; Petcher & Weber, 1974; Weber & Petcher, 1974; Quarles, Templeton & Zalkin, 1974; Gartland, Freeman & Bugg, 1974; Mostad & Römming, 1974; Ohki, Takenaka, Shimanouchi & Sasada, 1977; Ishida, Inoue, Fujiwara & Tomita, 1979).

Experimental. Pale-yellow transparent rods, specimen size $0.67 \times 0.30 \times 0.25$ mm. Data collected on a Stoe DIF4 four-circle diffractometer by $\omega/2\theta$ scan, scan width $1.05°$, scan speed 1.14–$3.42°$ min^{-1}. Three standard reflections were monitored every 90 min, intensity variation within 2%. Lattice parameters by

least-squares refinement of setting angles for 18 reflections, $15.42 \le \theta \le 24.49°$. 3496 reflections measured, max. $\sin\theta/\lambda = 0.6077$ Å^{-1}, $-8 \le h \le 8$, $-17 \le k \le 17$, $0 \le l \le 12$. Structure solved using *MITHRIL* (Gilmore, 1983). Anisotropic refinement minimizing $\sum w(\Delta F)^2$ with *SHELX*76 (Sheldrick, 1976), isotropic H atoms in geometrically fixed positions and with group temperature factors (five groups). H(1), on the indole N atom, was taken from the $\Delta\rho$ map and individually refined. $R = 0.0457$ and $wR = 0.0463$, $w = 1.2142/[\sigma^2(F) + 0.001F^2]$, for 1958 reflections with $F \ge 4\sigma(F)$ and 333 parameters. Max. $\Delta/\sigma = 0.020$ for any parameter. Max. and min. peaks in final $\Delta\rho$ map 0.24 and -0.23 e Å^{-3}. The inverse structure did not alter the R values. Atomic scattering factors from Cromer & Mann (1968) for C, O and N, and from Stewart, Davidson & Simpson (1965) for H atoms. Geometrical calculations by *PARST* (Nardelli, 1983).

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1,* main bond lengths and angles as well as hydrogen-bond data are given in Table 2. A *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule is shown in Fig. 1 together with the numbering scheme; the left-hand nitrobenzyl group has the same numbering as the right-hand group, but is primed. Fig. 2 illustrates the hydrogen-bond system in the direction of the *b* axis.

Table 1. *Atom coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
N1	0·6826 (7)	−0·0341 (4)	−0·0722 (4)	5·3 (2)
C2	0·5850 (8)	0·0030 (5)	0·0102 (5)	5·4 (2)
C3	0·6699 (7)	0·0814 (5)	0·0733 (4)	4·5 (2)
C3a	0·8257 (6)	0·0959 (5)	0·0284 (4)	3·9 (1)
C4	0·9633 (8)	0·1642 (5)	0·0565 (5)	5·0 (2)
C5	1·0994 (7)	0·1588 (5)	−0·0078 (5)	5·7 (2)
C6	1·1000 (8)	0·0853 (6)	−0·0957 (6)	6·4 (2)
C7	0·9662 (8)	0·0170 (6)	−0·1260 (5)	5·6 (2)
C7a	0·8286 (8)	0·0241 (5)	−0·0634 (5)	4·6 (2)
C8	0·6132 (7)	0·1374 (5)	0·1789 (5)	5·4 (2)
C9	0·7492 (7)	0·1258 (4)	0·3160 (4)	4·7 (2)
N10	0·7022 (5)	0·1843 (4)	0·4183 (4)	3·8 (1)
C11	0·5552 (7)	0·1369 (4)	0·4602 (5)	5·0 (2)
C11'	0·8633 (6)	0·2039 (5)	0·5332 (5)	4·7 (2)
C12	0·4788 (6)	0·1972 (4)	0·5526 (5)	3·8 (2)
C12'	0·8551 (6)	0·3023 (5)	0·5888 (5)	4·4 (2)
C13	0·3918 (6)	0·2833 (4)	0·5194 (4)	3·5 (2)
C13'	0·8324 (6)	0·3845 (5)	0·5101 (4)	4·8 (2)
C14	0·3295 (6)	0·3379 (5)	0·6071 (5)	4·5 (2)
C14'	0·8204 (8)	0·4740 (5)	0·5614 (9)	7·4 (3)
C15	0·3559 (8)	0·3036 (6)	0·7343 (6)	5·8 (2)
C15'	0·8378 (9)	0·4833 (7)	0·6934 (11)	9·2 (4)
C16	0·4404 (8)	0·2186 (6)	0·7714 (6)	6·4 (2)
C16'	0·8610 (8)	0·4046 (8)	0·7759 (8)	8·6 (3)
C17	0·5016 (7)	0·1664 (5)	0·6814 (6)	5·6 (2)
C17'	0·8668 (7)	0·3149 (6)	0·7211 (6)	6·2 (2)
N18	0·3537 (6)	0·3218 (5)	0·3824 (5)	5·1 (2)
N18'	0·8237 (7)	0·3783 (5)	0·3678 (5)	6·2 (2)
O19	0·3192 (6)	0·2687 (4)	0·2882 (4)	7·3 (2)
O19'	0·9347 (6)	0·3284 (4)	0·3360 (4)	6·5 (2)
O20	0·3572 (6)	0·4081 (5)	0·3722 (4)	8·7 (2)
O20'	0·7087 (7)	0·4242 (5)	0·2867 (5)	9·7 (2)

Table 2. *Bond distances (Å) and angles (°) for selected atoms and hydrogen-bond data (Å,°) with e.s.d.'s in parentheses*

N1—C2	1·391 (8)	C11—C12	1·519 (8)
N1—C7a	1·371 (8)	C11'—C12'	1·508 (9)
C2—C3	1·352 (9)	C12—C13	1·376 (8)
C3—C3a	1·418 (8)	C12'—C13'	1·399 (9)
C3—C8	1·515 (8)	C13—N18	1·479 (7)
C3a—C7a	1·396 (8)	C13'—N18'	1·470 (8)
C8—C9	1·526 (6)	N18—O19	1·202 (8)
C9—N10	1·471 (6)	N18—O20	1·218 (10)
N10—C11	1·480 (7)	N18'—O19'	1·220 (8)
N10—C11'	1·489 (5)	N18'—O20'	1·223 (8)
C2—N1—C7a	108·0 (5)	C9—N10—C11	109·1 (3)
N1—C2—C3	109·6 (6)	C11—N10—C11'	112·2 (3)
C2—C3—C8	125·4 (6)	N10—C11—C12	113·6 (4)
C2—C3—C3a	107·1 (5)	N10—C11'—C12'	111·4 (4)
C3a—C3—C8	127·4 (6)	C11—C12—C13	125·2 (4)
C3—C3a—C7a	107·4 (5)	C11'—C12'—C13'	122·8 (5)
C3—C3a—C4	133·6 (5)	C12—C13—N18	120·9 (5)
C4—C3a—C7a	118·9 (5)	C12'—C13'—N18'	120·5 (6)
C3a—C7a—C7	122·2 (6)	C13—N18—O19	120·2 (6)
N1—C7a—C7	129·9 (6)	C13—N18—O20	116·4 (5)
N1—C7a—C3a	107·9 (5)	O19—N18—O20	123·4 (5)
C3—C8—C9	111·4 (5)	C13'—N18'—O19'	118·2 (5)
C8—C9—N10	112·2 (4)	C13'—N18'—O20'	119·2 (6)
C9—N10—C11'	111·7 (3)	O19'—N18'—O20'	122·6 (6)
N(1)···O(20)ⁱ	3·165 (7)	H(1)···O(20')	2·55 (4)
N(1)···O(20')ⁱ	3·261 (7)	N(1)—H(1)···O(20)	124 (3)
H(1)···O(20)	2·47 (5)	N(1)—H(1)···O(20')	125 (3)

Symmetry code: (i) $-x+1, y-\tfrac{1}{2}, -z$.

The indole ring system is very nearly planar, the largest departure from the nine-atom least-squares plane being 0·013 (6) Å (C7a). The angle between the pyrrole and the benzene plane does not deviate significantly from zero. Bond lengths and angles are in

agreement with those previously published for tryptamines (*cf.* references above) and with the comparison of indole amines made by Falkenberg & Carlström (1971).

The N1—H1 distance in the pyrrole ring was refined to a value of 0·82 (5) Å, but was normalized (Taylor & Kennard, 1984) to 1·03 Å in the last refinement. The two benzyl groups form a pincer which opens up giving a dihedral angle of 24·2 (2)° between the benzene planes. When viewed orthogonally, the benzene planes do not fully overlap, this shift being due to a difference between the torsion angle C9—N10—C11—C12 and its primed opposite of 128·21 (5)°. The torsion angles for N10—C11—C12—C13 and its primed equivalent differ by 18·51 (7)°, indicating that the benzene planes are also non-parallel in the direction along the C12—C13 bond. The distances C12—C12' 3·175 (7), C13—C12' 3·441 (6) and C17—C17' 3·428 (9) Å are shorter than the van der Waals contact distance for aromatic rings, 3·54 Å, suggested by Bondi (1964). The nitro groups are twisted out of their benzene planes by 34·5 (5) and 45·8 (4)° (primed group) respectively. Both nitro groups participate in an intermolecular bifurcated hydrogen bond involving O20, O20' and H1 on the pyrrole amino group.
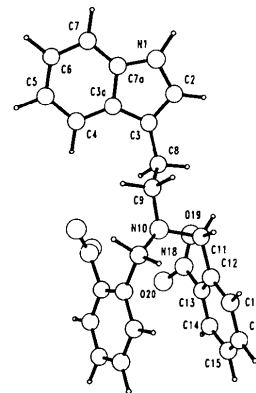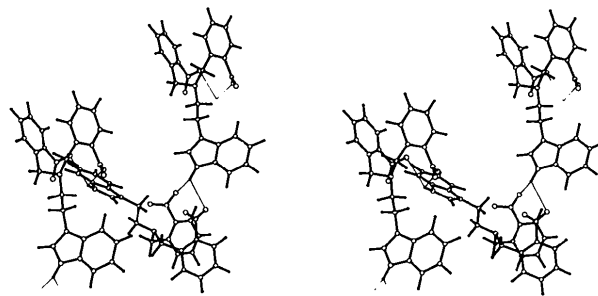

Fig. 1. Perspective view of the compound: the left-hand nitrobenzyl group has the same atomic numbering as the right-hand group, but primed.

Fig. 2. Stereographic projection showing the bifurcated hydrogen-bond system (thin lines) running along the *b* axis.

The hydrogen-bond lengths are longer for O20'—H1 (Table 2), which indicates a somewhat weaker bond for the primed nitrobenzyl group allowing a larger degree of freedom of movement for this group. In general the primed benzyl group has higher thermal motion (Table 1), supporting this assumption. Furthermore O19 and O19' form a short intramolecular contact with H11A and H11A', the distances being 2·36 (1) and 2·47 (1) Å, respectively.

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Structure of 4'-Acetoxy-3'-methoxycinnamic Acid

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Abstract. $C_{12}H_{12}O_5$, $M_r = 236\cdot23$, triclinic, $P\bar{1}$, $a = 9\cdot021$ (3), $b = 7\cdot987$ (3), $c = 9\cdot498$ (2) Å, $\alpha = 94\cdot24$ (2), $\beta = 106\cdot80$ (2), $\gamma = 114\cdot25$ (3)°, $V = 582\cdot5$ (4) Å³, $Z = 2$, $D_m = 1\cdot34$, $D_x = 1\cdot347$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu(\text{Mo } K\alpha) = 0\cdot0989$ mm⁻¹, $F(000) = 248$, $T = 293$ (1) K, $R = 0\cdot037$ for 1541 unique reflections. Hydrogen bonds are formed between terminal O and H atoms of adjacent molecules. The results prove that the dimer produced by mechanochemical reaction of 3,4-dimethoxycinnamyl alcohol is an *anti* head–tail cyclobutane dimer.

Introduction. Mechanochemical reaction products from crystalline 3,4-dimethoxycinnamyl alcohol have been found to contain a cyclobutane dimer (Lee, Tachibana & Sumimoto, 1988). To identify the stereochemical structure, crystalline 4'-acetoxy-3'-methoxycinnamic acid was submitted to a solid photodimerization. Reduction of the methyl ester of the acid with lithium aluminium hydride followed by methylation with dimethyl sulfate afforded the cyclobutane dimer, which was identical in all respects to the dimer obtained from the mechanochemical reaction products. According to Schmidt (1964), upon UV irradiation of cinnamic acid the α-form crystals give the *anti* head–tail cyclobutane dimer; by contrast the β-form crystals afford the *syn* head–head cyclobutane dimer. The stereochemical structure of the mechanochemically produced dimer should therefore be defined by the crystal structure of the title compound.

Experimental. The acid was prepared from vanillin by literature procedures (Adams & Bockstahler, 1952; Lee, Tachibana & Sumimoto, 1987). Colourless transparent crystal from methanol–water (2:1) solution. D_m by flotation in a mixture of *n*-hexane and carbon tetrachloride. Specimen (0·2 mm)³ mounted on Enraf–Nonius CAD-4 diffractometer, graphite-monochro-