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The use of restraints in Rietveld refinement of molecular compounds; a case study using the crystal structure determination of tryptamine free base

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The previously unknown crystal structure of the biogenic compound tryptamine, in the form of a free base ($C_{10}H_{12}N_2$), has been solved from X-ray powder diffraction data using simulated annealing followed by restrained Rietveld refinement [space group $P2_12_12_1$, $a = 12.28593$ (6), $b = 8.53351$ (4), $c = 8.49385$ (4) Å, $Z = 4$, final reduced-$\chi^2 = 5.255$]. A restrained Rietveld refinement was carried out in which the global weight factor, f, of the stereochemical restraints was gradually lowered. The effect of the relaxation of restraints on the crystal structure and on χ^2 was studied and a criterion for the final choice of f is reported. The crystal structure reported here shows efficient packing involving weak intermolecular hydrogen bonding and a herringbone-type packing pattern.

1. Introduction

Tryptamine is a biogenic serotonin-related indoamine and is the decarboxylation product of the amino acid tryptophan. Interest has recently focused on the role of tryptamine in a number of biological systems. For example, it is a neuroactive substance that may affect insect behaviour (Thomas *et al.*, 1998), and it may play a role in neuropsychiatric disorders such as stress or anxiety in the human brain (Mousseau & Butterworth, 1994; Medvedev *et al.*, 1995). The single-crystal structure of the compound has not been reported.

Traditional methods of molecular crystal structure solution from single-crystal diffraction data are often difficult to apply to powder diffraction data as a result of the inherent loss of information in a powder diffraction profile caused by peak overlap. Direct space methods can be used as a powerful alternative; for recent examples see Andreev *et al.* (1997), Dinnebier *et al.* (2000) and Kariuki *et al.* (1999). Direct space methods involve optimization of a trial structure, quantified by the quality of fit between the diffraction profile of the trial structure and the experimental diffraction profile.

Once a reasonable crystal structure model has been determined it is desirable to carry out a Rietveld refinement (Rietveld, 1969) of the structure, to improve the fit further and to optimize the structural information that can be derived. Rietveld refinement of molecular materials often involves a large number of stereochemical restraints that are necessary in order to maintain a physically reasonable structure. Restraints supplement the observed data and help maintain a reasonable data-to-parameter ratio. It has recently proved possible to carry out a refinement of a 1261-atom protein by incorporating a large number of restraints (Von Dreele, 1999).

Restraints are usually defined using an 'ideal' value together with an associated s.u. (standard uncertainty) for a given intramolecular parameter such as the length of a particular bond, the angle between two bonds or the planarity of the

constituents of an aromatic ring. Sometimes it is possible to remove the restraints during the final stages of a refinement. However, it may be desirable to leave the restraints in place in order to maintain an improved molecular geometry, although it is common to allow them to relax somewhat during refinement to allow the structure some freedom to move away from ideal values. The χ^2 function that quantifies the least-squares difference between observed and calculated data is minimized during refinement and incorporates a contribution from the profile and another from the restraints. Restrained Rietveld refinement is commonly used as the last stage of structure determination from powder data, but the weighting of the restraints against the data has not been widely discussed. This paper provides a study of the effect of the restraint weighting on the structure and on χ^2.

2. Structure solution and refinement

Tryptamine free base, 3-(2-aminoethyl)indole, Fig. 1, was purchased from Sigma Aldrich. The white powder (purity $\geq$ 99%) was ground and contained in a spinning 0.8 mm-diameter glass capillary during data collection. X-ray diffraction data were collected on diffractometer BM16 at the ESRF at room temperature, using a wavelength of 0.598542 (3) Å, to a maximum of 40° (2θ). The data were binned using a step size of 0.003° (2θ). Data in the region 10° to 40° (2θ) were counted for approximately 1.5 times longer than lower-angle data to improve the information content of the pattern with regard to structural detail.

The data were indexed using the first 22 peaks by the program *TREOR* (Werner *et al.*, 1985), showing that the cell is orthorhombic with lattice parameters a = 12.2787, b = 8.5309 and c = 8.4875 Å, with figures of merit $M(20)$ = 67 (De Wolff, 1968) and $F(20)$ = 391 (Smith & Snyder, 1979). An examination of systematic absences indicated that the space group is $P2_12_12_1$. A Pawley fit (Pawley, 1981) resulted in χ^2(Pawley) = 7.5.

Structure solution was carried out using a direct space method implemented using a simulated annealing approach (David *et al.*, 1998) in the program *DASH* (Cambridge Crystallographic Data Centre, 2001). An initial internal-coordinate description of the molecule was constructed. Two torsion angles, shown in Fig. 1, were allowed to vary freely, but all bond lengths and other angles were constrained to standard values. Twenty simulated annealing runs were carried out, all of which produced a crystal structure with realistic packing and a good fit between experimental and calculated profiles with χ^2(profile) $\simeq$ 21.8.

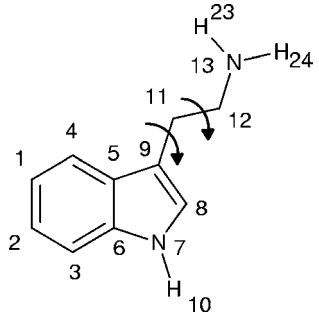

Figure 1
The atomic connectivity and numbering in the tryptamine molecule. H atoms bonded to C atoms are omitted for clarity. The arrows indicate torsion angles that were allowed to vary during simulated annealing.

A crystal structure solution with χ^2(profile) = 21.84 was used as the starting model for Rietveld refinement using the program *GSAS* (Larson & Von Dreele, 1994). Every bond length and angle in the molecule was defined and restrained using an ideal value and an associated s.u. The function that was minimized during the restrained refinement takes the form given in (1):

$$\chi^2_{\rm T} = \sum_j w_{yj}(y_{oj} - y_{cj})^2 + f\sum_{k=1}^{N_{\rm r}}(r_{ik} - r_{ck})^2/\sigma^2_{rk} = \chi^2_{\rm p} + \chi^2_{\rm r}. \quad (1)$$

The term $\chi^2_{\rm p}$ represents the standard Rietveld refinement minimization function, which is the contribution from the profile fit, where w_{yj} is the weight and y_{oj} and y_{cj} are observed and calculated intensities at each $2\theta_j$ position, respectively. The term $\chi^2_{\rm r}$ is the contribution from the restraints and is the sum over all restraints ($N_{\rm r}$ = total number of restraints), f is a global weight factor for the restraints, r_{ik} and r_{ck} are ideal and calculated values, respectively, for each restrained distance/angle, and σ_{rk} is the s.u. assigned to the ideal value for each restraint, k. Note that $\chi^2_{\rm r} = \chi^2_{\rm b} + \chi^2_{\rm a}$, where $\chi^2_{\rm b}$ is the contribution from bond-length restraints and $\chi^2_{\rm a}$ is the contribution from bond-angle restraints. Note also that $\chi^2_{\rm r} = fS_{\rm r}$, where $S_{\rm r}$ gives a measure of the square of the deviation from ideal values and is given in (2):

$$S_{\rm r} = \sum_{k=1}^{N_{\rm r}}(r_{ik} - r_{ck})^2/\sigma^2_{rk}. \quad (2)$$

The reduced-χ^2 is commonly used to measure the quality of a refinement and is given by $\chi^2_{\rm T}/(N_{\rm o} - P)$, where $N_{\rm o}$ is the number of observations (number of restraints plus number of data points in the profile) and P is the number of variable parameters.

Four independent searches of the April 2001 release of the Cambridge Structural Database (Allen & Kennard, 1993) were conducted in order to calculate ideal values and s.u. values to define restraints for all bond lengths and angles in the molecule. The fragments that were searched for, shown in Fig. 2, were chosen such that they were small enough to be well represented in the database (>100 occurrences) but large enough to be representative of a particular functional group within the target molecule. Each bond length and angle in the tryptamine molecule was represented in at least one of the four search fragments. The mean and standard deviation of the sample of representative bond lengths/angles taken from these searches were used to define an ideal value, $r_{\rm i}$, and an s.u., $\sigma_{\rm r}$, respectively, for each bond length/angle in the molecule. The parameters determined from each search are listed in Table 1 and the distance values are shown in Table 2. Using the CSD to derive ideal values is particularly effective for identifying

Table 1
Search details.

Atomic numbering is shown in Fig. 1.

Search	Number of fragments found	Bond distances	Bond angles
1	1267 structures (1875 fragments)	C1—C2 C2—C3 C3—C6 C6—C5 C5—C4 C4—C1 C1—H16 C2—H15 C3—H14 C4—H20	C4—C1—C2 C4—C1—H16 H16—C1—C2 C1—C2—C3 C1—C2—H15 H15—C2—C3 C2—C3—C6 C2—C3—H14 H14—C3—C6 C3—C6—C5 C6—C5—C4 C5—C4—C1 C5—C4—H20 H20—C4—C1
2	236 structures (278 fragments)	C5—C6 C6—N7 N7—C8 C8—C9 C9—C5 N7—H10 C8—H17 C9—C11	C9—C5—C6 C5—C6—N7 C6—N7—C8 C6—N7—H10 H10—N7—C8 N7—C8—C9 N7—C8—H17 H17—C8—C9 C8—C9—C5 C8—C9—C11 C11—C9—C5 C3—C6—N7 C4—C5—C9
3	96 structures (170 fragments)	C12—N13 N13—H23 N13—H24 C12—H21 C12—H22	C12—N13—H23 C12—N13—H24 H23—N13—H24 H21—C12—N13 H21—C12—H22 H22—C12—N13 C11—C12—N13 C11—C12—H21 C11—C12—H22
4	94 structures (127 fragments)	C11—C12 H18—C11 H19—C11	C9—C11—C12 C9—C11—H18 C9—C11—H19 H18—C11—H19 C12—C11—H18 C12—C11—H19

subtle structural characteristics, such as alternating C—C distances in an aromatic ring, and this approach has been used previously (Nowell *et al.*, 2002).

It should be noted that when a bond-length or angle restraint is defined using a sample of crystal structures taken from the CSD, there are three factors affecting the size of its s.u. The first is a result of the chemical variation in bond lengths and angles caused by differences in physical interactions between atoms in different materials, the second is the result of errors on atom positions located during structure determination, and the third is the sample size. It is particularly important to consider the second factor for bonds involving H atoms, since the majority of structures stored in the CSD are X-ray studies where the positions of H atoms may be ill defined. For this reason, the s.u. values used in the definition of two bond-length restraints involving H atoms (N7—H10 and C8—H17) were reduced to 0.06 Å from values of 0.09 Å and 0.07 Å, respectively, based on the distribution of values in the CSD.

A 12-term linear-interpolation background function, lattice parameters, zero point and peak shapes were refined in the Rietveld fit. The peak shape consisted of a Lorentzian $X\tan\theta$ contribution (Thompson *et al.*, 1987), where X is the refined variable, convoluted with an asymmetry correction (Finger *et al.*, 1994) where the ratio S/L was refined ($2S$ is the sample height and L is the distance from sample to detector). Subsequently, isotropic atomic displacement parameters for non-H atoms (constrained to be equal for atoms of the same element) and positions of all 24 atoms were refined subject to the restraints described. The preferred orientation along the [100] axis was also modelled giving a small value for the refined coefficient.

Initially strong restraints ($f = 1000$) were used to ensure stability. f was reduced stepwise until finally the restraints were removed ($f = 0$). The effect of this relaxation on the crystal structure and on χ^2 was investigated.

3. Results and discussion

The effect of f on the intramolecular geometry of tryptamine has been studied. S_r was calculated and is plotted as a function of f ($0 \leq f \leq 100$) in Fig. 3. Clearly S_r increases as the restraints are relaxed, indicating the increase in deviation of calculated bond lengths and angles from ideal values as f is lowered. It is important to remember that the restraints used in this refinement are not self-consistent as they were derived from a large number of known structures and there was no attempt to impose self-consistency by optimizing the values for the tryptamine molecule. Therefore, the ideal values cannot all be met exactly simultaneously, and as $f \rightarrow \infty$, S_r tends towards a minimum value, $S_r(\text{min})$, where $S_r(\text{min}) > 0$. S_r reaches a maximum value of 584 at $f = 0$; this corresponds to a mean

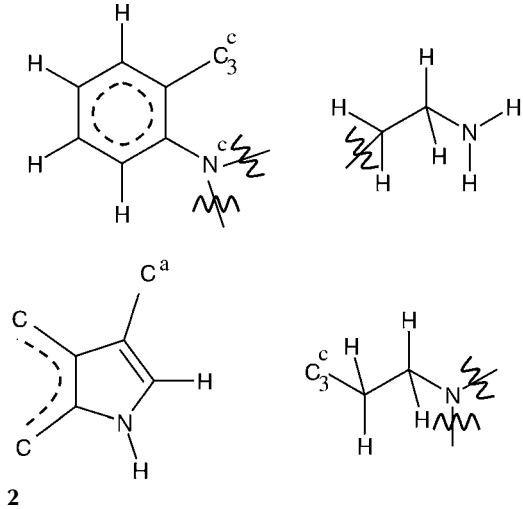

Figure 2
The search fragments used to determine ideal bond lengths, angles and s.u. values to define restraints for use in refinement. The superscript 'a' or 'c' indicates an acyclic or cyclic atom, respectively; the subscript '3' indicates the attachment of three atoms.

Table 2
Bond-length restraints and calculated values at $f = 0$, $f = 65$ and $f = 1000$.

	Restraint values		$f = 0$		$f = 65$		$f = 1000$	
Bond	r_i (Å)	σ_r (Å)	r_c (Å)	$(r_i - r_c)^2/\sigma_r^2$	r_c (Å)	$(r_i - r_c)^2/\sigma_r^2$	r_c (Å)	$(r_i - r_c)^2/\sigma_r^2$
C1—C2	1.39	0.02	1.38 (1)	0.250	1.396 (4)	0.090	1.393 (1)	0.023
C2—C3	1.38	0.02	1.38 (1)	0.000	1.370 (4)	0.250	1.381 (1)	0.003
C3—C6	1.39	0.02	1.39 (1)	0.000	1.400 (4)	0.250	1.390 (1)	0.000
C6—C5	1.41	0.02	1.445 (9)	3.063	1.412 (4)	0.010	1.407 (1)	0.023
C5—C4	1.40	0.02	1.332 (9)	11.560	1.391 (4)	0.203	1.399 (1)	0.003
C4—C1	1.37	0.02	1.38 (1)	0.250	1.373 (4)	0.023	1.371 (1)	0.003
C6—N7	1.37	0.01	1.38 (1)	1.000	1.372 (2)	0.040	1.3695 (7)	0.003
N7—C8	1.37	0.02	1.40 (1)	2.250	1.358 (4)	0.360	1.368 (1)	0.010
C8—C9	1.36	0.01	1.372 (9)	1.440	1.362 (3)	0.040	1.3610 (7)	0.010
C9—C5	1.43	0.02	1.466 (9)	3.240	1.440 (4)	0.250	1.434 (1)	0.040
C9—C11	1.50	0.02	1.49 (1)	0.250	1.496 (4)	0.040	1.501 (1)	0.003
C11—C12	1.51	0.02	1.54 (1)	2.250	1.520 (4)	0.250	1.513 (1)	0.023
C12—N13	1.44	0.06	1.410 (9)	0.250	1.432 (6)	0.018	1.447 (3)	0.014
C1—H16	0.98	0.06	0.96 (4)	0.111	0.96 (2)	0.111	0.978 (4)	0.001
C2—H15	0.98	0.06	0.80 (5)	9.000	0.95 (2)	0.250	0.976 (4)	0.004
C3—H14	0.98	0.06	0.79 (5)	10.028	0.97 (2)	0.028	0.979 (4)	0.000
C4—H20	0.98	0.06	1.13 (5)	6.250	0.99 (2)	0.028	0.980 (4)	0.000
N7—H10	0.93	0.06	0.51 (7)	49.000	0.87 (2)	1.000	0.926 (4)	0.004
C8—H17	0.99	0.06	0.95 (5)	0.444	0.96 (2)	0.250	0.988 (4)	0.001
C11—H18	1.00	0.06	1.11 (4)	3.361	1.00 (2)	0.000	0.998 (4)	0.001
C11—H19	0.99	0.06	0.86 (4)	4.694	0.98 (2)	0.028	0.990 (4)	0.000
C12—H21	0.98	0.04	0.94 (5)	1.000	0.98 (1)	0.000	0.980 (3)	0.000
C12—H22	0.98	0.04	1.11 (5)	10.563	1.00 (1)	0.250	0.982 (3)	0.003
N13—H23	0.91	0.06	1.15 (5)	16.000	0.94 (2)	0.250	0.911 (4)	0.000
N13—H24	0.91	0.06	1.01 (5)	2.778	0.94 (2)	0.250	0.913 (4)	0.003

$(r_i - r_c)^2/\sigma_r^2$ value of 8.7 for all bond lengths and angles in the unrestrained structure. When $(r_{ik} - r_{ck})^2/\sigma_{rk}^2 = 8.7$ for a restraint k, the difference between ideal and calculated values is less than three times the restraint s.u. Nineteen of the 25 bond lengths and 33 of the 42 bond angles in the unrestrained structure are within 3 s.u. of their ideal value [*i.e.* $(r_i - r_c)^2/\sigma_r^2 < 9$]. All bond angles and all but one of the bond lengths that are outside this range involve an H atom. Details of bond lengths in the unrestrained structure are given in Table 2; details regarding bond angles have been provided as supplementary information.[1]

There is an indication of some structural stability even when the restraints are removed. However, it was considered necessary to use $f > 0$ for the final stages of refinement of the structure reported here in order to achieve a realistic crystal structure, particularly with respect to H-atom positions. In order to allow the restrained structure some freedom and simultaneously achieve a physically reasonable crystal structure, it was considered appropriate to allow the restraints to relax as much as possible while ensuring that all bond lengths and angles are within 1 s.u. of their ideal value, *i.e.* $(r_{ik} - r_{ck})^2/\sigma_{rk}^2 \leq 1$ for each restraint k. The lowest value of f in this study at which $(r_i - r_c)^2/\sigma_r^2 \leq 1$ for all bond lengths and angles is $f = 65$. Therefore, during refinement of the final structure reported here, the global weight factor for the restraints was relaxed from $f = 1000$ to $f = 65$. The final fit between experimental and calculated profiles for this structure is presented in Fig. 4. Refinement details are presented in Table 3.

Comparing the structure refined using $f = 1000$ with the final structure (refined using $f = 65$), the mean shift in atomic

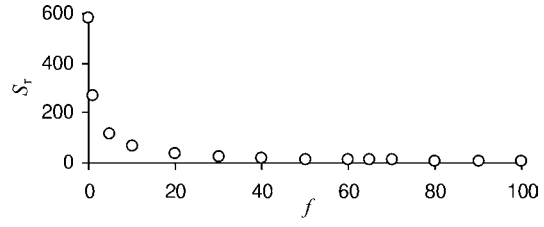

Figure 3
Variation of S_r in the region $0 \leq f \leq 100$.

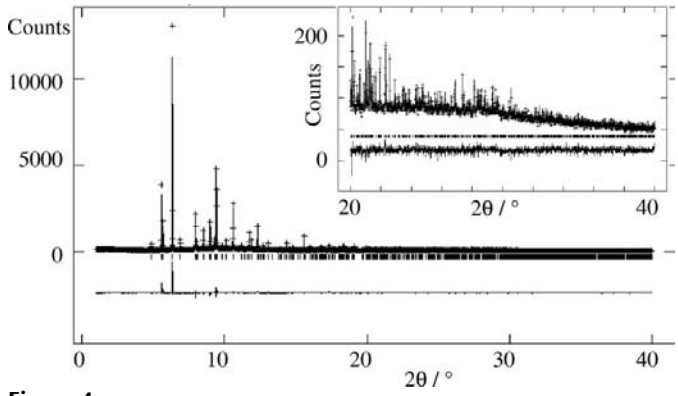

Figure 4
The final fit between experimental and calculated diffraction profiles after refinement of the structure reported here using $f = 65$.

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0051). Services for accessing these data are described at the back of the journal.

Table 3
Refinement details.

$2\theta_{min}$ (°)	1
$2\theta_{max}$ (°)	40
Step size (°)	0.003
λ (Å)	0.598542 (3)
Number of *hkl* reflections	831
Total number of observations	13068
Number of profile points	13001
Number of bond-length restraints	25
Number of bond-angle restraints	42
Number of parameters: profile	20
Number of parameters: atom	74
Global weight factor on restraints	65
Space group	$P2_12_12_1$
Z	4
a, b, c (Å)	12.28593 (6), 8.53351 (4), 8.49385 (4)
V (Å^3)	890.51 (1)
U_{iso} (Å^2)	C 0.0464 (7), N 0.051 (1), H 0.025
Preferred orientation	[100] axis ratio 1.049 (3)
R_{wp}	0.0815
R_p	0.0656
$R_F{}^2$	0.1446
Reduced-χ^2	5.255
Profile contribution to reduced-χ^2	5.227
χ^2_r	712.32
χ^2_b	261.97
χ^2_a	450.35

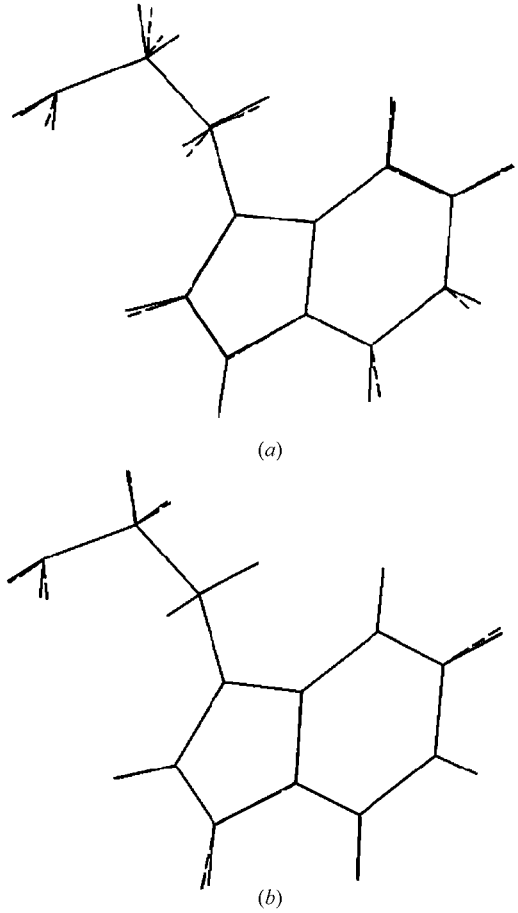

Figure 5
(*a*) The overlay of the structure refined using $f = 0$ (dashed lines) with that refined using $f = 65$ (solid lines). (*b*) The overlay of the structure refined using $f = 65$ (solid lines) with that refined using $f = 1000$ (dashed lines). This is the view along the *b* axis.

position is 0.02 Å for non-H atoms and 0.07 Å for H atoms. Comparing the structure refined using $f = 65$ with that refined using $f = 0$, the mean shift is 0.03 Å for non-H atoms and 0.26 Å for H atoms. Fig. 5 enables visual comparison of these structures. The non-H atoms move by relatively small amounts compared with the extremely weakly scattering H atoms, whose positions are clearly unstable in the absence of information complementary to the X-ray diffraction data. Calculated bond lengths for the $f = 0$, $f = 65$ and $f = 1000$ structures are listed in Table 2; calculated angles for these structures have been provided as supplementary information.

The choice of the final value of f in this refinement was governed by the maximum value of $(r_i - r_c)^2/\sigma_r^2$ for all bond lengths and angles in the molecule. It should be noted that other criteria could be used for the choice of f. It is important, however, to maintain a balance between very weak and very strong restraints. In the former case, the restraints have so little influence on the molecular structure that the differences between ideal and calculated values are large relative to restraint s.u. values, and it is likely that some atom positions (particularly H-atom positions) will become physically unreasonable. In the latter case, the deviation from ideal values is minimal even at the expense of the profile fit.

The effect of f on χ^2_b, χ^2_a and χ^2_r has been studied and is plotted in Fig. 6. χ^2_b and χ^2_a vary quite differently with f. Both tend towards zero as $f \rightarrow 0$, but χ^2_b reaches a maximum at $f = 10$, decays rapidly towards a minimum in the region of $f = 400$ and then increases slowly for $400 < f < 1000$. χ^2_a has no stationary points and increases continuously for $0 < f < 1000$. At $50 < f < 70$, the total contribution from the restraints (χ^2_r) reaches a local minimum.

The initial plateau in χ^2_r that begins at $f \simeq 15$ (see Fig. 6) may be related to the size of the sampling step in the profile. The observed quantities in the powder data that affect the internal coordinates are the *hkl* intensities, which are represented in the powder data using profile points at equally spaced 2θ intervals. In this case, the data were binned using a step size of 0.003° (2θ), and there are 13001 profile points and 831 *hkl* reflections; as a result, there are an average of 15.6 profile points for each reflection, so the sampling step is corrected for when f reaches this value.

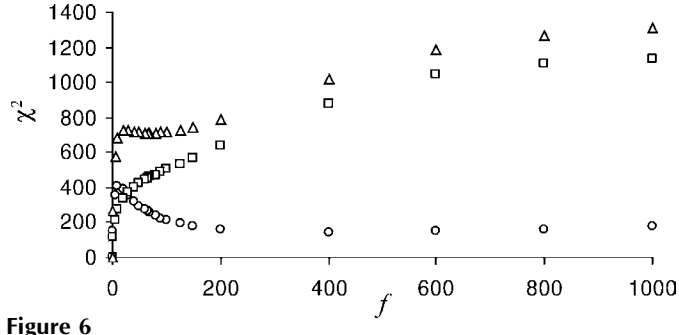

Figure 6
Contributions towards χ^2 values made by stereochemical restraints as a function of their global weight factor. Circles represent the contribution made by the bond-length restraints (χ^2_b), squares represent the contribution made by the bond-angle restraints (χ^2_a), while triangles represent the total contribution made by both sets of restraints (χ^2_r).

The molecules in the structure form a distinctive herringbone packing pattern, shown in Fig. 7. The molecules align so that the H atoms in the *meta* and *para* positions to the indole point towards the π-electron density of the six-membered ring on an adjacent molecule. Intermolecular hydrogen bonding is apparent between the N—H group of the indole and the N atom of the primary amine, also shown in Fig. 7. The N···(H—)N distance is 2.92 Å and the N···H—N angle is 139°; these intermolecular values were unrestrained during refinement and comparable structures in the CSD indicate that they are realistic.

4. Conclusion

The crystal structure of the biologically important tryptamine molecule has been determined. Stepwise relaxation of restraints during refinement enabled determination of an objective criterion for the final value of the stereochemical restraint global weight factor, f, for the structure reported here. Changes in molecular structure and trends in the behaviour of χ^2 values as a function of f have been reported.

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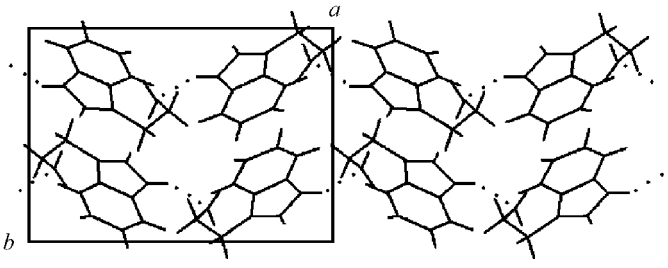

Figure 7
The view along c of the herringbone packing pattern in the refined crystal structure. The dotted lines represent intermolecular hydrogen bonds between the N—H group of the indole and the N atom of the primary amine. The contents of two unit cells are shown.

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