L-Tryptophan 4-nitrophenol trisolvate

V. H. Rodrigues, M. M. R. R. Costa, M. Belsley and E. de Matos Gomes

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The title compound, C_{11}H_{12}N_{2}O_{2}·3C_{6}H_{5}NO_{3}, comprises a zwitterionic amino acid formed by two nearly planar groups: (i) the indole ring and C\(_{\alpha}\) and (ii) the carboxyl group, C\(_{\alpha}\), as well as the amine N atom, with r.m.s. deviations of 0.0084 and 0.0038 Å, respectively. The angle between these idealized planes is 39.47 (9)°. The amine group of the amino acid is in a syn (\(-\)) arrangement relative to the ring system. The overall crystal structure results from the packing of sheets parallel to the (001) planes. These sheets are formed by a pair of screw axis related parallel networks bound by hydrogen-bond and \(\pi\)-\(\pi\) stacking interactions. The intermolecular cohesion of all organic residues in each of the latter two-dimensional networks is achieved via strong hydrogen bonding, nitro-\(\pi\) and \(\pi\)-\(\pi\) stacking interactions.

**Related literature**

For a general review on nonlinear optical properties of organic molecules and crystals, see: Chemla & Zyss (1987); Zyss & Ledoux (1994); Zyss & Nicoud (1996). For similar and most common conformations of \(\tau\)-tryptophan, see: Bye et al. (1973); Bakke & Mostad (1980). For the Cambridge Structural Database, see: Allen (2002). For information on optical second harmonic generation (SHG) measurements, see: Kurtz & Perry (1968).

**Experimental**

**Crystal data**

- \(\text{C}_{11}\text{H}_{12}\text{N}_{2}\text{O}_{2}·3\text{C}_{6}\text{H}_{5}\text{NO}_{3}\)
- \(M_r = 621.56\)
- Monoclinic, \(P_2_1\)
- \(a = 13.0321 (9)\) Å
- \(b = 6.7332 (4)\) Å
- \(c = 17.3091 (10)\) Å
- \(\beta = 104.479 (3)\)
- \(V = 1470.59 (16)\) Å\(^3\)
- \(Z = 2\)
- \(\text{Mo Kα radiation}\)
- \(\mu = 0.11\) mm\(^{-1}\)
- \(T = 291\) K
- \(0.3 \times 0.2 \times 0.15\) mm

**Data collection**

- Bruker–Nonius APEXII CCD area-detector diffractometer
- Absorption correction: multi-scan
- (SADABS, Sheldrick, 2003)
- \(\bar{T}_{\text{min}} = 0.915, \bar{T}_{\text{max}} = 0.980\)
- 94463 measured reflections
- 4289 independent reflections
- 410 parameters

**Refinement**

- \(R(F^2) = 0.035\)
- \(wR(F^2) = 0.101\)
- \(S = 1.04\)
- 4289 reflections
- 410 parameters

**Table 1**

| D–H···A | D–H | H···A | D···A | D–H···A |
|---------|------|-------|-------|--------|
| N1–H1B···O21 | 0.89 | 2.10 | 2.970 | 165 |
| N1–H1C···O1" | 0.89 | 1.86 | 2.743 | 172 |
| O43–H4A···O2a" | 0.82 | 1.81 | 2.623 | 171 |
| O23–H23A···O3ii | 0.82 | 2.08 | 2.820 | 150 |
| O33–H33A···O2ii" | 0.82 | 1.98 | 2.687 | 170 |

Symmetry codes: (i) \(x+1, y, z\); (ii) \(-x+1, y-1/2, -z\); (iii) \(-x, y-1, z\); (iv) \(x-1, y, z\).

**Data collection:** APEX2 (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHLEX97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FK2052).

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supplementary materials

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Comment

Non-linear optical phenomena (NLO) form the basis for a wide range of devices including frequency doublers, electro-optic modulators, optical limiters, high speed optical gates and parametric amplifiers. Organic molecules containing \( \pi \) electron systems asymetrized by donor and acceptor groups are highly polarizable entities which may give rise to organic polar crystals for NLO applications. The properties of individual molecules and their organization in the bulk crystalline structure are the key factors that determine the properties of the resulting molecular materials. An essential condition to obtain even-order NLO processes in materials is a noncentrosymmetric crystal structure. However, optimal molecular orientations are required if appreciable effects are to be achieved in molecular materials (Chemla & Zyss, 1987; Zyss & Ledoux, 1994; Zyss & Nicoud, 1996). In this context the crystal structure of the title compound resulting from co-crystallization of a chiral molecule, \( \text{L-tryptophan} \), and \( \text{p-nitrophenol} \), which has a high ground state dipole moment is reported. No other crystal structures with three neutral independent \( \text{p-nitrophenol} \) molecules were found in a search to the CSD database, version 1.13 (Allen, 2002).

The aminoacid is a zwitterion with overall neutral charge, which means that no Brønsted-Lowry acid-base reaction has occurred between \( \text{L-tryptophan} \) and \( \text{p-nitrophenol} \) molecules; this is further confirmed by inspection and comparison of all three C–O distances of the \( \text{p-nitrophenol} \) molecules which range from 1.341 (3) Å to 1.351 (3) Å.

The \( \text{L-tryptophan} \) has a conformation similar to the one found in the \( \text{L-form of DL-formate} \) (Bye et al., 1973), with the amine group in a syn (-sc) arrangement relative to the indole and, as in most cases (Bakke & Mostad, 1980), with C1 trans to C4. The zwitterion can be divided in two planar groups forming an angle of 39.47 (9)°. The first group consists of the indole ring and C3; the second group includes the carboxyl group and the amine N atom. Root mean square deviations of the atoms in these latter planes are 0.0084 and 0.0038 Å, respectively.

Hydrogen bonded two-dimensional networks, parallel to the (001) planes, involving all four independent molecules, can be found in the crystal structure of the title compound. Figure 2 shows such a two-dimensional network of H-bonded, nitro-\( \pi \) and \( \pi-\pi \) stacked molecules. In the latter networks, chains formed by the aminoacid and one \( \text{p-nitrophenol} \) (X41—X46, where \( X \) stands for C, N or O) running along the \( a \) axis can be found. These chains are linked through two H-bonds: N1—H1A···O41 or N1—H1A···O42 and O43—H43A···O2a. Other chains, formed by the same aminoacid and \( \text{p-nitrophenol} \) molecules, with a more irregular shape, run along the \( b \) axis and are also connected through two H-bonds: the same bifurcated N1—H1A···O41 or N1—H1A···O42 and N2—H2A···O42. The other two \( \text{p-nitrophenol} \) molecules (X21—X26 and X31—X36, where \( X \) stands for C, N or O) can be seen as dimmers, H-bonded via O23—H23A···O32, that connect to the latter described base of perpendicularly running chains through H-bonds N1—H1B···O21, N2—H2A···O22 and O33—H33···O24. All but one of the H-bonds found are used to build the two-dimensional network, which includes all the molecules present in the asymmetric unit. Nitro-\( \pi \) and \( \pi-\pi \) interactions further stabilize the stacking of the latter dimmers and the indole ring along the \( a \) axis, via N31—O31···Cg21—C26, N21—O21···Cgpyrrole, N21—O21···Cgnd.benz and correspondent \( \pi-\pi \) intermolecular contacts. Geometric details of the \( \pi-\pi \) and nitro-\( \pi \) interactions can be found in tables A
and B. An H-bonded and also π-π stacked pair of the latter two-dimensional networks (screw axis related to each other), constitutes a sheet (parallel to the (001) planes); the relevant intermolecular contacts in the binding of this pair of neighbouring two-dimensional networks are the H-bond N1–H1C···O1ii and π-π stacking interactions Cgind.benz···CgC21—C26vi and CgC41—C6vi···CgC41—C46vii (geometric details can be found in table A). The overall three-dimensional structure can be viewed as a repetition along the c axis of the latter sheets, as shown in Fig. 3.

Optical second harmonic generation (SHG) was measured on polycrystalline samples using the standard Kurtz and Perry technique (Kurtz and Perry, 1968). The material was particle sized using a set of standard microsieves (Retsch) having mesh width between 50 µm and 160 µm. The sample cell consisted of a microscope slide with a depression of 3 mm diameter and 0.5 mm thickness covered with a flat microscope slide. The generated second harmonic signal was compared with that generated by polycrystalline urea with the same grain size and similar sample preparation. The L-tryptophan tris(4-nitrophenol) SHG response was twice that of urea.

Symmetry codes: (i) x, y + 1, 1 - z; (ii) -x + 1, y - 1/2, -z; (iii) x, y - 1, z; (iv) x + 1, y, z; (v) -x + 1, y + 1/2, -z + 1; (vi) -x, y + 1/2, -z.

Experimental

Single crystals were produced by dissolving 5.0 mmol of L-tryptophan and 10 mmol of p-nitrophenol in 30 ml of hot methanol. Yellow needles were formed by slow cooling at room temperature.

Refinement

The structure was solved by direct methods using SHELXS97 (Sheldrick, 2008). All H(C/N) atoms were placed at idealized positions and refined as riding [C—H=0.93 (aromatic C)— 0.98Å, Uiso(H)=1.2 Ueq(C); N—H=0.89Å and Uiso(H)=1.5 Ueq(N) (amino N), N—H=0.86Å and Uiso(H)=1.2 Ueq(N) (aromatic N)]. Hydroxyl H atoms have been positioned and refined using HFIX 147 with SHELXL (Sheldrick, 2008).

Examination of the crystal structure with PLATON (Spek, 2009) showed that there are no solvent-accessible voids in the crystal lattice.

The refined model structure is non-centrosymmetric with only atoms which are poor anomalous scatterers for the wavelength used, therefore Friedel pairs were merged before the final refinement.

Computing details

Data collection: APEX2 (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT (Bruker, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: SHELXL97 (Sheldrick, 2008).
Figure 1

ORTEPII (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% level.

Figure 2

Representation of the two-dimensional networks, paralell to the (001) planes, of H-bonded molecules. Different sorts of chains can be individualized. Nitro-π and π-π stacking are also evident.
Figure 3
ac face view, showing the layered packing along the c axis of the two-dimensional networks parallel to (001) (shown in Fig. 2). H-bonded and π–π stacked pairs of screw axis related networks are visible.

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Crystal data

C_{11}H_{12}N_{2}O_{2}·3C_{6}H_{5}NO_{3}

$M_r = 621.56$

Monoclinic, $P2_1$

Hall symbol: $P 2yb$

$a = 13.0321 (9)$ Å

$b = 6.7332 (4)$ Å

$c = 17.3091 (10)$ Å

$\beta = 104.479 (3)^\circ$

$V = 1470.59 (16)$ Å\(^3\)

$Z = 2$

$F(000) = 648$

$D_x = 1.404$ Mg m\(^{-3}\)

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 8205 reflections

$\theta = 2.6$–25.8\(^\circ\)$

$\mu = 0.11$ mm\(^{-1}\)$

$T = 291$ K

Block, yellow

$0.3 \times 0.2 \times 0.15$ mm
supplementary materials

Data collection

Bruker–Nonius APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

\( \varphi \) and \( \omega \) scans

Absorption correction: multi-scan

\( \text{SADABS} \); Sheldrick, 2003

94463 measured reflections

4289 independent reflections

2984 reflections with \( I > 2\sigma(I) \)

\( R_{\text{int}} = 0.031 \)

\( \theta_{\text{max}} = 30.9^\circ \), \( \theta_{\text{min}} = 3.2^\circ \)

\( T_{\text{min}} = 0.915 \), \( T_{\text{max}} = 0.980 \)

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\( R[F^2 > 2\sigma(F^2)] = 0.035 \)

\( wR(F^2) = 0.101 \)

\( S = 1.04 \)

4289 reflections

410 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

\( \Delta \rho_{\text{max}} = 0.14 \) e Å\(^{-3} \)

\( \Delta \rho_{\text{min}} = -0.15 \) e Å\(^{-3} \)

Special details

Geometry. All e.s.d.’s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.’s are taken into account individually in the estimation of e.s.d.’s in distances, angles and torsion angles; correlations between e.s.d.’s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.’s is used for estimating e.s.d.’s involving l.s. planes.

Refinement. Refinement of \( F^2 \) against ALL reflections. The weighted \( R \)-factor \( wR \) and goodness of fit \( S \) are based on \( F^2 \), conventional \( R \)-factors \( R \) are based on \( F \), with \( F \) set to zero for negative \( F^2 \). The threshold expression of \( F^2 > \sigma(F^2) \) is used only for calculating \( R \)-factors(gt) etc. and is not relevant to the choice of reflections for refinement. \( R \)-factors based on \( F^2 \) are statistically about twice as large as those based on \( F \), and \( R \)-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å\(^2\))

| Atom | \( x \) | \( y \) | \( z \) | \( U_{\text{iso}}^*/U_{eq} \) |
|------|---------|---------|---------|------------------|
| O1   | 0.53801 (10) | 1.2043 (3) | 0.02152 (8) | 0.0593 (4) |
| O2   | 0.68508 (10) | 1.2042 (3) | 0.12018 (8) | 0.0595 (4) |
| C1   | 0.59036 (14) | 1.1548 (3) | 0.08874 (11) | 0.0431 (4) |
| C2   | 0.53789 (12) | 1.0190 (3) | 0.13787 (10) | 0.0387 (4) |
| H2   | 0.5327 | 1.0894 | 0.1863 | 0.046* |
| N1   | 0.42901 (10) | 0.9709 (3) | 0.08966 (9) | 0.0411 (3) |
| H1A  | 0.3969 | 1.0818 | 0.0683 | 0.062* |
| H1B  | 0.3921 | 0.9159 | 0.1209 | 0.062* |
| H1C  | 0.4330 | 0.8864 | 0.0510 | 0.062* |
| C3   | 0.60036 (14) | 0.8278 (3) | 0.16154 (11) | 0.0457 (4) |
| H3A  | 0.6082 | 0.7614 | 0.1136 | 0.055* |
| H3B  | 0.6707 | 0.8611 | 0.1933 | 0.055* |
| C4   | 0.55002 (14) | 0.6876 (3) | 0.20785 (11) | 0.0441 (4) |
| C5   | 0.48396 (16) | 0.5339 (3) | 0.17877 (11) | 0.0507 (5) |
| H5   | 0.4631 | 0.4972 | 0.1253 | 0.061* |
| N2   | 0.45239 (15) | 0.4408 (3) | 0.23941 (10) | 0.0573 (4) |
| H2A  | 0.4110 | 0.3396 | 0.2342 | 0.069* |
|     |  
|-----|-------------------------------------|
| C6  | 0.49761 (16)  
| C7  | 0.48737 (19)  
| H7  | 0.4465  
| C8  | 0.5409 (2)  
| H8  | 0.5356  
| C9  | 0.6023 (2)  
| H9  | 0.6372  
| C10 | 0.61303 (18)  
| H10 | 0.6552  
| C11 | 0.55904 (15)  
| O41 | 0.24461 (14)  
| O42 | 0.25999 (13)  
| N41 | 0.20582 (15)  
| C41 | 0.09109 (14)  
| C42 | 0.02939 (15)  
| H42 | 0.0606  
| C43 | −0.07909 (15)  
| H43 | −0.1217  
| C44 | −0.12507 (14)  
| O43 | −0.23142 (11)  
| H43A| −0.2510  
| C45 | −0.06176 (15)  
| H45 | −0.0927  
| C46 | 0.04710 (15)  
| H46 | 0.0901  
| O21 | 0.29993 (15)  
| O22 | 0.3440 (2)  
| N21 | 0.30274 (16)  
| C21 | 0.25695 (16)  
| C22 | 0.21164 (19)  
| H22 | 0.2096  
| C23 | 0.1695 (2)  
| H23 | 0.1380  
| C24 | 0.17371 (18)  
| O23 | 0.13486 (17)  
| H23A| 0.0916  
| C25 | 0.2203 (2)  
| H25 | 0.2238  
| C26 | 0.2620 (2)  
| H26 | 0.2929  
| O31 | 1.00715 (17)  
| O32 | 1.01880 (18)  
| N31 | 0.98754 (16)  
| C31 | 0.92836 (16)  
| C32 | 0.88446 (16)  
| H32 | 0.8918  
| C33 | 0.82972 (17)  
| H33 | 0.7998  
| C34 | 0.81888 (17)  

*supplementary materials*
supplementary materials

|       | U^11   | U^22   | U^33   | U^12   | U^13   | U^23   |
|-------|--------|--------|--------|--------|--------|--------|
| O1    | 0.0484 (7) | 0.0692 (10) | 0.0588 (8) | −0.0064 (7) | 0.0106 (6) | 0.0227 (8) |
| O2    | 0.0432 (7) | 0.0694 (11) | 0.0653 (8) | −0.0176 (7) | 0.0121 (6) | −0.0004 (8) |
| O33   | 0.76777 (16) | 0.2709 (3) | 0.27645 (11) | 0.0824 (5) |
| H33A  | 0.7372 | 0.2606 | 0.2291 | 0.124* |
| C35   | 0.8646 (2) | 0.5020 (5) | 0.36739 (14) | 0.0821 (8) |
| H35   | 0.8588 | 0.4191 | 0.4091 | 0.098* |
| C36   | 0.9181 (2) | 0.6787 (5) | 0.38391 (14) | 0.0752 (7) |
| H36   | 0.9469 | 0.7177 | 0.4364 | 0.090* |

Atomic displacement parameters (Å^2)

Acta Cryst. (2012). E68, o920
supplementary materials

| Atom  | U(111) | U(220) | U(330) | U(440) | U(550) | U(660) |
|-------|--------|--------|--------|--------|--------|--------|
| C33   | 0.0567 | 0.0565 | 0.0488 | 0.0055 | 0.0082 | −0.0017|
| C34   | 0.0574 | 0.0571 | 0.0605 | −0.0010| 0.0135 | 0.0004 |
| O33   | 0.0906 | 0.0718 | 0.0788 | −0.0230| 0.0102 | 0.0056 |
| C35   | 0.108  | 0.086  | 0.0551 | −0.0258| 0.0252 | 0.0055 |
| C36   | 0.0945 | 0.0815 | 0.0515 | −0.0182| 0.0219 | −0.0084|

Geometric parameters (Å, °)

| Bond  | Distance (Å) | Angle (°) |
|-------|--------------|-----------|
| O1—C1 | 1.238 (2)     |           |
| O2—C1 | 1.263 (2)     |           |
| C1—C2 | 1.522 (2)     |           |
| C2—N1 | 1.491 (2)     |           |
| C2—C3 | 1.524 (3)     |           |
| C2—H2 | 0.9800        |           |
| N1—H1A| 0.8900        |           |
| N1—H1B| 0.8900        |           |
| N1—H1C| 0.8900        |           |
| C3—C4 | 1.492 (3)     |           |
| C3—H3A| 0.9700        |           |
| C3—H3B| 0.9700        |           |
| C4—C5 | 1.360 (3)     |           |
| C4—C11| 1.438 (3)     |           |
| C5—N2 | 1.371 (3)     |           |
| C5—H5 | 0.9300        |           |
| N2—C6 | 1.367 (3)     |           |
| N2—C6 | 0.8600        |           |
| C6—C7 | 1.396 (3)     |           |
| C6—C11| 1.407 (3)     |           |
| C7—C8 | 1.374 (4)     |           |
| C7—H7 | 0.9300        |           |
| C8—C9 | 1.379 (5)     |           |
| C8—H8 | 0.9300        |           |
| C9—C10| 1.384 (3)     |           |
| C9—H9 | 0.9300        |           |
| C10—C11| 1.393 (3)    |           |
| C10—H10| 0.9300       |           |
| O41—N41| 1.223 (3)    |           |
| O42—N41| 1.217 (3)    |           |
| N41—C41| 1.455 (3)    |           |
| C41—C42| 1.375 (3)    |           |
| C41—C46| 1.379 (3)    |           |
| C42—C43| 1.375 (3)    |           |
| C42—H42| 0.9300       |           |
| C43—C44| 1.385 (3)    |           |
| C43—H43| 0.9300       |           |
| O1—C1—O2 | 125.70 (17) |           |
| O1—C1—C2 | 117.88 (15) |           |
| O2—C1—C2 | 116.40 (16) |           |
| N1—C2—C1 | 108.38 (14) |           |
N1—C2—C3 109.67 (15)  O43—C44—C45 123.14 (17)
C1—C2—C3 111.92 (13)  C43—C44—C45 120.04 (17)
N1—C2—H2 108.9  C46—C45—H45 120.0
C1—C2—H2 108.9  C46—C45—H46 120.0
C3—C2—H2 108.9  C46—C45—H45 120.0
C2—N1—H1A 109.5  C44—C45—C46 118.87 (17)
C2—N1—H1B 109.5  C44—C45—H45 120.6
H1A—N1—H1B 109.5  C44—C45—H46 120.6
C2—N1—H1C 109.5  H1A—N1—H1C 109.5
H1A—N1—H1C 109.5  H1B—N1—H1C 109.5
C4—C3—C2 113.69 (14)  O22—N21—O21 118.6 (2)
C4—C3—H3A 108.8  O22—N21—C21 118.6 (2)
C2—C3—H3A 108.8  C22—C21—C26 121.1 (2)
C4—C3—H3B 108.8  C22—C21—N21 120.0 (2)
C2—C3—H3B 108.8  C26—C21—N21 120.0 (2)
H3A—C3—H3B 107.7  C22—C21—H22 120.0
C5—C4—C11 106.28 (17)  C21—C22—C26 122.2 (3)
C5—C4—C3 127.24 (17)  C21—C22—H22 120.0
C11—C4—C3 126.45 (18)  C22—C21—N21 120.0 (2)
C4—C5—H5 124.8  C23—C22—C21 119.5 (2)
N2—C5—H5 124.8  C23—C22—H22 120.0
N2—C6—C11 125.6  C24—C23—C22 119.5 (2)
N2—C6—C7 125.6  C24—C23—H23 120.0
C6—C7—C8 121.8  C24—O23—H23A 109.5
C7—C8—C9 121.8  C24—C25—C26 120.5 (2)
O23—C24—C23 122.2 (2)
C8—C9—C10 121.5 (3)  C25—C24—C23 120.0 (2)
C8—C9—H9 121.5 (3)  C25—C24—C25 117.8 (2)
C9—C10—C11 119.2  C25—C24—H25 119.8
C9—C10—H10 119.2  C26—C25—C24 120.5 (2)
C11—C10—H10 119.2  C26—C25—H25 119.8
C6—C7—H7 118.9  C26—C25—H26 120.7
C7—C8—C9 118.9  C21—C26—C25 118.6 (2)
C8—C9—H9 118.9  C21—C26—H26 120.7
C9—C8—C7 121.5 (3)  O31—N31—O32 119.0 (2)
C9—C8—H8 121.5 (3)  O31—N31—C31 122.4 (2)
C8—C9—C10 119.2  O32—N31—C31 119.0 (2)
C9—C10—C11 118.3 (3)  O32—N31—C31 119.0 (2)
C9—C10—H10 118.3 (3)  C33—C32—C31 119.7 (2)
C11—C10—H10 118.3 (3)  C33—C32—H32 120.2
C10—C11—C6 118.99 (19)  C33—C32—H32 120.2
C10—C11—C4 134.3 (2)  C31—C32—H32 120.2
C6—C11—C4 106.74 (17)  C32—C33—C34 120.3 (2)
O42—N41—O41 122.2 (2)  C32—C33—H33 119.8
O42—N41—C41 118.7 (2)  C34—C33—H33 119.8
O41—N41—C41 119.1 (2)  C34—C33—H33 119.8
C42—C41—C46 121.78 (17)  O33—C34—C35 119.9 (2)
C42—C41—N41 118.93 (19)  O33—C34—H33A 119.9 (2)
C41—C46—C45 120.0 (2)  C34—O33—H33A 109.5
C42—C41—C6 118.93 (19)  C36—C35—C34 120.8 (2)
C42—C41—N41 118.93 (19)  C36—C35—H35 119.6
C46—C45—H45 120.0
supplementary materials

| Bond                  | Angle (°)   | Bond                  | Angle (°)   |
|-----------------------|-------------|-----------------------|-------------|
| C46—C41—N41          | 119.28 (19) | C34—C35—H35          | 119.6       |
| C43—C42—C41          | 119.08 (18) | C35—C36—C31          | 118.9 (2)   |
| C43—C42—H42          | 120.5       | C35—C36—H33          | 120.6       |
| C41—C42—H42          | 120.5       | C31—C36—H36          | 120.6       |

| Bond                  | Angle (°)   | Bond                  | Angle (°)   |
|-----------------------|-------------|-----------------------|-------------|
| O1—C1—C2—N1          | 1.2 (2)     | C42—C43—C44—O43      | 179.9 (2)   |
| O2—C1—C2—N1          | −177.61 (17)| C42—C43—C44—C45     | −0.2 (3)    |
| O1—C1—C2—C3          | 122.22 (19) | O43—C44—C45—C46     | −178.8 (2)  |
| O2—C1—C2—C3          | −56.5 (2)   | C43—C44—C45—C46     | 1.3 (3)     |
| N1—C2—C3—C4          | −58.0 (2)   | C44—C45—C46—C41     | −0.8 (3)    |
| C1—C2—C3—C4          | −178.34 (15)| C42—C41—C46—C45     | −0.8 (3)    |
| C2—C3—C4—C5          | 94.3 (2)    | N41—C41—C46—C45     | −179.85 (19)|
| C2—C3—C4—C11         | −83.3 (2)   | O22—N21—C21—C22     | −179.2 (2)  |
| C11—C4—C5—N2         | −1.0 (2)    | O21—N21—C21—C22     | −0.7 (3)    |
| C3—C4—C5—N2          | −179.01 (18)| O22—N21—C21—C26     | −1.2 (4)    |
| C4—C5—N2—C6          | 0.5 (2)     | O21—N21—C21—C26     | 177.3 (2)   |
| C5—N2—C6—C7          | 178.8 (2)   | C26—C21—C22—C23     | 0.8 (4)     |
| C5—N2—C6—C11         | 0.3 (2)     | N21—C21—C22—C23     | 178.8 (2)   |
| N2—C6—C7—C8          | −178.4 (2)  | C21—C22—C23—C24     | −0.7 (4)    |
| C11—C6—C7—C8         | −0.1 (3)    | C22—C23—C24—O23     | −178.8 (3)  |
| C6—C7—C8—C9          | −0.4 (4)    | C22—C23—C24—C25     | −0.1 (4)    |
| C7—C8—C9—C10         | 0.1 (5)     | O23—C24—C25—C26     | 179.7 (3)   |
| C8—C9—C10—C11        | 0.7 (4)     | C23—C24—C25—C26     | 0.9 (4)     |
| C9—C10—C11—C6        | −1.2 (3)    | C22—C21—C26—C25     | −0.1 (4)    |
| C9—C10—C11—C4        | 179.4 (2)   | N21—C21—C26—C25     | −178.0 (2)  |
| N2—C6—C11—C10        | 179.5 (2)   | C24—C25—C26—C21     | −0.8 (4)    |
| C7—C6—C11—C10        | 0.9 (3)     | O31—N31—C31—C36     | 170.9 (3)   |
| N2—C6—C11—C4         | −0.9 (2)    | O32—N31—C31—C36     | −6.9 (3)    |
| C7—C6—C11—C4         | −179.5 (2)  | O31—N31—C31—C32     | −8.5 (3)    |
| C5—C4—C11—C10        | −179.3 (2)  | O32—N31—C31—C32     | 173.7 (2)   |
| C3—C4—C11—C10        | −1.3 (4)    | C36—C31—C32—C33     | −0.4 (3)    |
| C5—C4—C11—C6         | 1.2 (2)     | N31—C31—C32—C33     | 179.0 (2)   |
| C3—C4—C11—C6         | 179.19 (18)| C31—C32—C33—C34     | −0.2 (3)    |
| O42—N41—C41—C42      | 174.3 (2)   | C32—C33—C34—O33     | −178.9 (2)  |
| O41—N41—C41—C42      | −6.6 (3)    | C32—C33—C34—C35     | −0.2 (3)    |
| O42—N41—C41—C46      | −6.7 (3)    | O33—C34—C35—C36     | 179.9 (3)   |
| O41—N41—C41—C46      | 172.5 (2)   | C33—C34—C35—C36     | 1.1 (4)     |
| C46—C41—C42—C43      | 1.9 (3)     | C34—C35—C36—C31     | −1.7 (5)    |
| N41—C41—C42—C43      | −179.0 (2)  | C32—C31—C36—C35     | 1.3 (4)     |
| C41—C42—C43—C44      | −1.4 (3)    | N31—C31—C36—C35     | −178.1 (2)  |

Hydrogen-bond geometry (Å, °)

| D—H···A              | D—H | H···A | D···A  | D—H···A |
|----------------------|-----|------|-------|---------|
| N1—H1B···O21         | 0.89| 2.10 | 2.970 (2)| 165     |
| N1—H1C···O1i         | 0.89| 1.86 | 2.743 (2)| 172     |
| O43—H43A···O2ii      | 0.82| 1.81 | 2.623 (2)| 171     |

Acta Cryst. (2012). E68, o920
supplementary materials

O23—H23A···O32ii 0.82 2.08 2.820 (3) 150
O33—H33A···O2iii 0.82 1.88 2.687 (2) 170

Symmetry codes: (i) −x+1, y−1/2, −z; (ii) x−1, y−1, z; (iii) x, y, z.

Geometric parameters of short ring-interactions with centroid to centroid distances less than 6.0 Å.

| Cg1···Cg4     | Cg−Cg(Å) | α(°)  |
|---------------|----------|-------|
| Cg1···Cg5     | 4.6231 (14) | 14.12 (12) |
| Cg2···Cg4     | 4.3316 (15) | 11.22 (13) |
| Cg2···Cg4i    | 5.9401 (15) | 65.16 (13) |
| Cg2···Cg5     | 4.6336 (14) | 14.58 (12) |
| Cg4···Cg5i    | 4.3160 (14) | 17.89 (12) |
| Cg5···Cg6ii   | 5.8571 (13) | 61.42 (11) |
| Cg6···Cg6iv   | 3.5724 (12) | 4.92 (2) |

Notes: α is the dihedral angle between interacting planes; Cg1 is the centroid of the pyrrole ring; Cg2 is the centroid of the benzene indole ring; Cg4 is the centroid of C21 to C26 π-ring; Cg5 is the centroid of C31 to C36 π-ring; Cg6 is the centroid of C41 to C46 π-ring. Symmetry codes: (i) 1-x,-1/2+y,1-z; (ii) -1+x,y,z; (iii) 1+x,y,z; (iv) -x,1/2+y,-z

Geometric parameters of N-O···Cg(π-ring) interactions with O···Cg less than 4.0 Å.

| N21—O21···Cg1 | O···Cg(Å) | N···O···Cg(°) | N···Cg(Å) |
|---------------|----------|---------------|----------|
| N21—O22···Cg2 | 3.821 (3) | 74.05 (16)    | 3.678 (2) |
| N31—O31···Cg4iii | 3.954 (2) | 67.54 (15)    | 3.665 (2) |

Notes: The centroids and symmetry codes are as in table A.