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(*E*)-2-Methyl-3-(2-methyl-2-nitrovinyl)-1*H*-indole and (*E*)-3-(2-methyl-2-nitrovinyl)-2-phenyl-1*H*-indole

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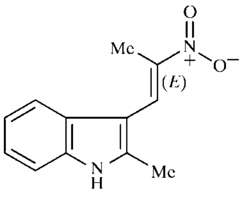
In the title compounds, $C_{12}H_{12}N_2O_2$, (I), and $C_{17}H_{14}N_2O_2$, (II), respectively, the indole rings are planar and the vinyl groups lie out of the indole planes, making dihedral angles of 33.48 (5) and 41.31 (8)°, respectively. In (II), the dihedral angle between the phenyl and indole ring planes is 32.06 (6)°. In both molecules, the double bond connecting the methylnitrovinyl group and the indole nucleus adopts an *E* configuration. Notwithstanding the differences in space group [$C2/c$ for (I) and $P2_12_12_1$ for (II)], the mode of packing of compounds (I) and (II) is determined by similar intermolecular N—H···O hydrogen-bonding interactions, forming chains that run parallel to [101] in (I) and [001] in (II).

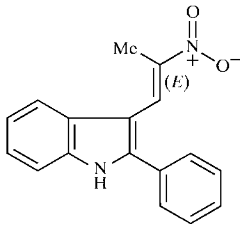
Comment

3-(2-Nitrovinyl)indoles are very important synthons for the preparation of tryptamines (Shen *et al.*, 1998) in high yield. They also undergo Michael addition reactions, resulting in the formation of a wide range of indole derivatives (Chakrabarty *et al.*, 2001). Apart from their synthetic utility, 3-(2-nitrovinyl)indoles also exhibit amebicidal (Sharma *et al.*, 1987) and antifungal (Canoira *et al.*, 1989) activity. We have synthesized a series of 3-(2-nitrovinyl)indoles and evaluated them for antitubercular activity (Sonar & Crooks, unpublished work).

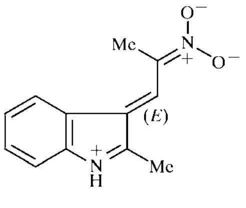
The title compounds, (I) and (II), were prepared by condensation of 2-methylindole-3-carbaldehyde and 2-phenylindole-3-carbaldehyde with nitroethane in the presence of ammonium acetate, to afford (*E*)-2-methyl-3-(2-methyl-2-nitrovinyl)-1*H*-indole, (I), and (*E*)-3-(2-methyl-2-nitrovinyl)-2-phenyl-1*H*-indole, (II), each as a single geometrical isomer. The structures of products (I) and (II) were initially identified by NMR spectroscopy. Generally, condensation reactions of indole-3-carbaldehydes with nitromethane or nitroethane afford the corresponding *E* isomer. However, when a nitrovinyl group containing an ester functionality in the 2-position is utilized in these types of reactions, the reaction affords a mixture of *Z* and *E* isomers (Bakhmutov *et al.*, 1977). In order to confirm the double-bond geometry of the title compounds, and to obtain more detailed information on the conformations of these molecules in the solid state, their X-ray structure determination has been carried out and the results are presented here.



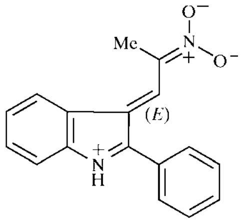
(I)



(II)



(I*a*)



(II*a*)

Figs. 1 and 2 illustrate the molecular structures and atom-numbering schemes for (I) and (II), respectively. For ease of comparison, the two compounds are discussed in parallel below. Selected geometric parameters are presented in Tables 1 and 3 for (I) and (II), respectively. For each structure, the indole ring is planar, with bond distances and angles comparable with those reported for other indole derivatives (Mason *et al.*, 2003). Compounds (I) and (II) are *E* isomers, and the N2—C10 bond is in a *trans* disposition with respect to the C2—C9 bond. In both compounds, deviations from the ideal bond angle of 120° are observed in the bond angles C2=C1—C12, C2—C9=C10, C9=C10—C11, C9=C10—N2 and N2—C10—C11. While the N1—C1—C12 and C1=C2—C9 bond angles are close to the ideal value, the C2—

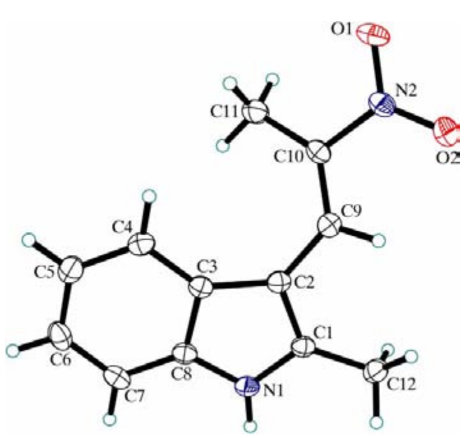


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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C9═C10—N2 torsion angle indicates that the nitrovinyl group is nearly planar [177.96 (11)° in (I) and 178.86 (18)° in (II)], and the plane of the nitrovinyl group is twisted, by 33.48 (5)° for (I) and 41.31 (8)° for (II), with respect to the indole ring plane. However, comparing the C2—C9 bond length [1.4335 (17) Å in (I) and 1.451 (3) Å in (II)] with the standard value for a single bond connecting a C_{ar} atom to a Csp^2 atom [1.470 (15) Å; Wilson, 1992] suggests that the indole system has an extended conjugation through the ethylene double bond and the nitro group. There is further evidence for this in the shortening of the N1—C1 and N2—C10 and lengthening of the C1═C2 and C9═C10 bonds compared with reported values similar to the N1—C1 and N2—C10 bonds for other compounds (Mason *et al.*, 2003; Strauss *et al.*, 2003). In the case of (II), the phenyl group at the 2-position makes a dihedral angle of 32.06 (6)° with the plane of the indole ring. This extended conjugation suggests that compounds (I) and (II) exist predominantly in resonance forms (I*a*) and (II*a*), respectively, which explains the highly coloured and crystalline nature of the title compounds, due to the extended chromophore, and the increased polarity within these molecules. Furthermore, the absence of IR absorption bands at 1550 and 1372 cm^{-1}, which is typical of the nitro group in 3-(2-nitrovinyl)indoles (Bucki & Mark, 1977), the appearance of two new bands between 1300 and 1250 cm^{-1}, and the intense UV absorption near 400 nm, confirm the existence of resonance forms (I*a*) and (II*a*).

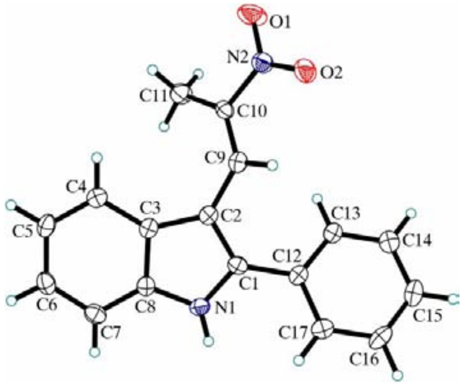

Figure 2
A view of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

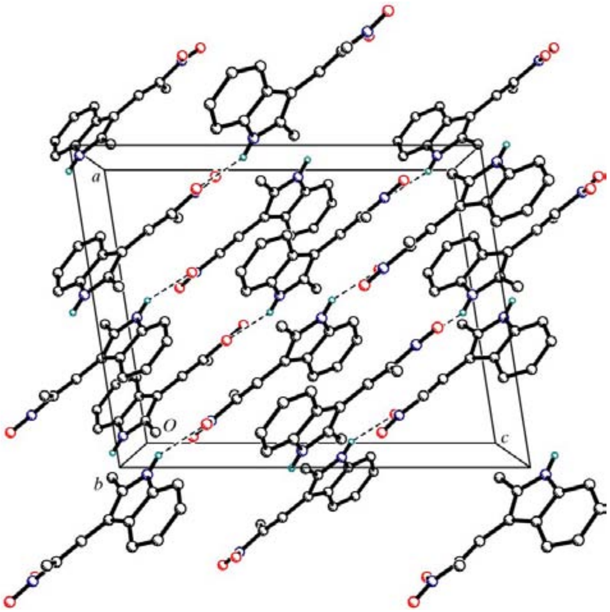

Figure 3
The crystal structure of (I), viewed along the *b* axis.

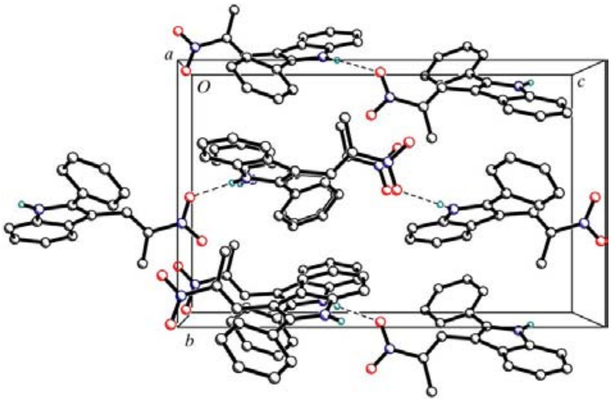

Figure 4
The crystal structure of (II), viewed along the *a* axis.

The packing of compounds (I) and (II), as viewed along the *b* and *a* axes, is illustrated in Figs. 3 and 4, respectively. In each, atom H1 participates in a weak intermolecular N1—H1···O2 interaction [symmetry code ($\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$) for (I) and ($\frac{1}{2}-x$, $-y$, $\frac{1}{2}+z$) for (II)], linking the title compounds into chains that run parallel to [101] and [001], respectively.

Experimental

For the preparation of (I), solid ammonium acetate (0.3 g, 3.8 mmol) was added to a suspension of 2-methylindole-3-carbaldehyde (1.08 g, 6.8 mmol) in nitroethane (3 ml). The mixture was stirred vigorously under reflux at 393–403 K for 2 h. The mixture was then cooled, and the solid which appeared was collected by filtration. Recrystallization from methanol afforded orange–brown crystals of (I) suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$): δ 2.26 (*s*, 3H), 2.42 (*s*, 3H), 7.11 (*pd*, 2H), 7.37 (*dd*, 1H), 7.47 (*dd*, 1H), 8.28 (*s*, 1H), 11.92 (*s*, 1H); ^{13}C NMR ($CDCl_3$): δ 12.6, 15.8, 105.3, 111.5, 119.4, 120.3, 121.7, 125.6, 129.1, 135.9, 141.5, 145.6. For the preparation of (II), solid ammonium acetate (0.3 g, 3.8 mmol) was added to a suspension of 2-phenylindole-3-carbaldehyde (1.5 g, 6.8 mmol) in nitroethane (3 ml). The mixture was stirred vigorously under reflux at 393–403 K for 2 h. The mixture was then cooled and the solid which appeared was collected by filtration. Recrystallization from methanol afforded orange–brown crystals of (II) suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$): δ 2.22 (*s*, 3H), 7.20 (*m*, 2H), 7.58 (*m*, 7H), 8.17 (*s*, 1H), 12.28 (*s*, 1H); ^{13}C NMR ($CDCl_3$): δ 15.7, 105.0, 112.1, 120.0, 120.7, 122.7, 125.9, 128.7, 128.9, 129.2, 131.0, 136.5, 141.2, 144.0.

Compound (I)

Crystal data

$C_{12}H_{12}N_2O_2$
$M_r = 216.24$
Monoclinic, $C2/c$
$a = 12.1176$ (3) Å
$b = 11.3888$ (3) Å
$c = 15.2667$ (4) Å
$\beta = 98.8372$ (10)°
$V = 2081.87$ (9) Å^3
$Z = 8$

$D_x = 1.380$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2484 reflections
$\theta = 1.0$–27.5°
$\mu = 0.10$ mm^{-1}
$T = 90.0$ (2) K
Block, orange–brown
0.40 × 0.35 × 0.30 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans at fixed $\chi = 55°$
4507 measured reflections
2390 independent reflections
1927 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.019$
$\theta_{\rm max} = 27.5°$
$h = -15 \rightarrow 15$
$k = -13 \rightarrow 14$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.114$
$S = 1.10$
2390 reflections
147 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 0.7762P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

N1—C1	1.3534 (16)	C9—C10	1.3532 (17)
N1—C8	1.3803 (16)	C10—N2	1.4484 (15)
C1—C2	1.4015 (17)	N2—O1	1.2400 (14)
C1—C12	1.4833 (18)	N2—O2	1.2416 (14)
C2—C9	1.4335 (17)		
C1—N1—C8	110.29 (10)	C9—C10—N2	116.25 (12)
N1—C1—C12	120.70 (11)	C9—C10—C11	129.54 (11)
C2—C1—C12	130.12 (12)	N2—C10—C11	113.95 (11)
C1—C2—C9	121.00 (11)	O1—N2—O2	121.27 (11)
C10—C9—C2	129.02 (12)	O1—N2—C10	117.80 (11)
C12—C1—C2—C9	−0.4 (2)	C2—C9—C10—N2	177.96 (11)
C1—C2—C9—C10	154.03 (13)	C9—C10—N2—O2	3.40 (16)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2$^{\rm i}$	0.88	2.22	3.0112 (14)	150

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

Compound (II)

Crystal data

$C_{17}H_{14}N_2O_2$
$M_r = 278.30$
Orthorhombic, $P2_12_12_1$
$a = 7.7856$ (2) Å
$b = 10.4801$ (3) Å
$c = 16.7489$ (5) Å
$V = 1366.61$ (7) Å^3
$Z = 4$
$D_x = 1.353$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1825 reflections
$\theta = 1.0$–27.5°
$\mu = 0.09$ mm^{-1}
$T = 90.0$ (2) K
Block, orange–brown
0.25 × 0.22 × 0.22 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω scans at fixed $\chi = 55°$
3128 measured reflections
3128 independent reflections
2257 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.058$
$\theta_{\rm max} = 27.5°$
$h = -10 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.106$
$S = 1.04$
3128 reflections
192 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.018 (3)
Absolute structure: Flack (1983), with 1319 Friedel pairs
Flack parameter: 0.4 (16)

Table 3
Selected geometric parameters (Å, °) for (II).

N1—C1	1.371 (2)	C9—C10	1.340 (3)
N1—C8	1.376 (2)	C10—N2	1.454 (2)
C1—C2	1.386 (3)	N2—O1	1.232 (2)
C1—C12	1.466 (3)	N2—O2	1.242 (2)
C2—C9	1.451 (3)		
C1—N1—C8	109.50 (17)	C9—C10—N2	115.80 (18)
N1—C1—C12	121.03 (17)	C9—C10—C11	129.37 (18)
C2—C1—C12	129.75 (17)	N2—C10—C11	114.72 (17)
C1—C2—C9	121.72 (18)	O1—N2—O2	122.01 (17)
C10—C9—C2	128.36 (19)	O1—N2—C10	117.76 (17)
C12—C1—C2—C9	−6.7 (3)	C2—C9—C10—N2	178.86 (18)
C1—C2—C9—C10	144.4 (2)	C9—C10—N2—O2	−2.9 (3)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2$^{\rm i}$	0.88	2.11	2.953 (2)	161

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

The refinement of structure (I) required no particular special treatment. However, for structure (II), which is an all-light-atom achiral molecule that happened to crystallize in space group $P2_12_12_1$, the Friedel opposites were not merged and the structure was refined as an inversion twin. Not surprisingly, the Flack (1983) parameter [0.4 (16)] was wholly inconclusive, and for this reason the twin fractions were fixed at 50:50 for the final stages of refinement. An alternative treatment involving refinement against a data set where the Friedel pairs had been merged led to some small differences; the largest Fourier difference map features were marginally smaller (0.18 and −0.20 e Å^{-3} *versus* 0.19 and −0.21 e Å^{-3} for the unmerged data), the value of R_1 was smaller (0.041 *versus* 0.044), and the s.u. values were larger by a factor of around 1.3, which is approximately the square root of the ratio of the numbers of data present in each set. The H atoms in structures (I) and (II) were found in difference Fourier maps and subsequently refined either using riding models, in which the H-atom coordinates were determined geometrically from their attached parent atom, or by placing them at positions of maximal threefold average electron density calculated within the toroid of possible H-atom positions for those H atoms on methyl groups attached to sp^2 carbons. Bond distances for H atoms were fixed as follows: aromatic C—H = 0.95 Å, methyl C—H = 0.98 Å and N—H = 0.88 Å. Isotropic displacement parameters for the H atoms were defined as $1.2U_{\rm eq}$ for aromatic CH and NH, and $1.5U_{\rm eq}$ for methyl CH_3.

For both compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1995); publication software: *SHELXL97* and local procedures.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1609). Services for accessing these data are described at the back of the journal.

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