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# Two 9-[(*E*)-nitrophenylvinyl]-9*H*-carbazoles

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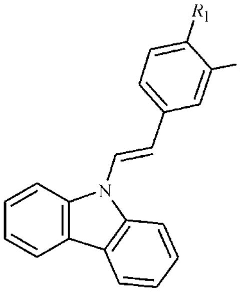
The crystal structures of 9-[(*E*)-(4-nitrophenyl)vinyl]-9*H*-carbazole and 9-[(*E*)-(3-nitrophenyl)vinyl]-9*H*-carbazole, both $C_{20}H_{14}N_2O_2$, are determined mainly by van der Waals forces and $\pi$–$\pi$ interactions between the carbazole and benzene systems. However, the packing modes are different. In the 4-nitro derivative, the molecules in the weakly bound stack are related by a unit-cell translation, while in the 3-nitro derivative there are centrosymmetric pairs of molecules joined by $\pi$–$\pi$ interactions and also pairs of molecules, related by another centre of symmetry, connected by eight relatively short C—H···O interactions.

## Comment

Over the past few years, vigorous growth has been observed in the chemistry of carbazole derivatives due to their electroactivity and luminescent properties (Grazulevicius *et al.*, 2003, and references therein; Hyun *et al.*, 2006). These compounds are thermally and photochemically stable, which makes them useful materials for technological applications. For instance, the carbazole ring is easily funtionalized and covalently linked to other molecules (Diaz *et al.*, 2002). This enables its use as a convenient building block for the design and synthesis of molecular glasses, which are widely studied as components of electroactive and photoactive materials (Zhang *et al.*, 2004). The high photoconductivities and hole-transporting properties of many polymeric materials can be greatly improved by incorporating carbazole as a pendant group in the framework. This molecule, with a $\pi$-conjugated system, is used as a host material for both small-molecule OLEDs (organic light-emitting diodes) and polymer PLEDs (polymer light-emitting diodes) due to its high triplet energy and good hole-transporting ability (see, for example, Chen *et al.*, 2003). PLEDs can emit white (Paik *et al.*, 2002), pure deep-blue (Lu *et al.*, 2004) or green or red (Zhang *et al.*, 2006) light. Further extension of the $\pi$-conjugated double-bond system has been obtained *via* the synthesis of *N*-nitrostyryl-substituted carbazole derivatives, which are interesting from the photochemical point of view (Prukała *et al.*, 2007). We report here the crystal and molecular structures of two such derivatives, *viz*. the *p*-nitro isomer 9-[(*E*)-(4-nitrophenyl)vinyl]-9*H*-carbazole, (I), and the *m*-nitro isomer 9-[(*E*)-(3-nitrophenyl)vinyl]-9*H*-carbazole, (II).



(I) $R_1$=NO$_2$, $R_2$=H
(II) $R_1$=H, $R_2$=NO$_2$

The bond angles within the nitrophenyl ring are influenced by the presence of the substituents. The nitro group causes an increase in the angle at the point of substitution and a decrease in the neighbouring angles. The effect of the vinyl group is the reverse (*cf.* Domenicano, 1988). The final bond-angle pattern is close to an additive combination of these effects (Table 1). It might be noted, however, that other factors (*e.g.* crystal packing) also influence the bond angles; otherwise, for instance, the bond angles in (I) should be symmetrically distributed.

The conformation of the molecules of (I) and (II) (Figs. 1 and 2, respectively) can be described by the dihedral angles between the approximately planar fragments of the carbazole ring system, the bridging vinyl group, the nitrophenyl ring and the nitro group (Table 2). In (I), the whole nitrostyryl group is close to planarity [maximum dihedral angle = 5.6 (3)°], but it is significantly twisted with respect to the carbazole group [17.4 (2)°]. The whole of compound (II) is almost planar, with the largest dihedral angle of 8.3 (3)° being observed between the nitrophenyl ring and nitro-group planes. Interestingly, the

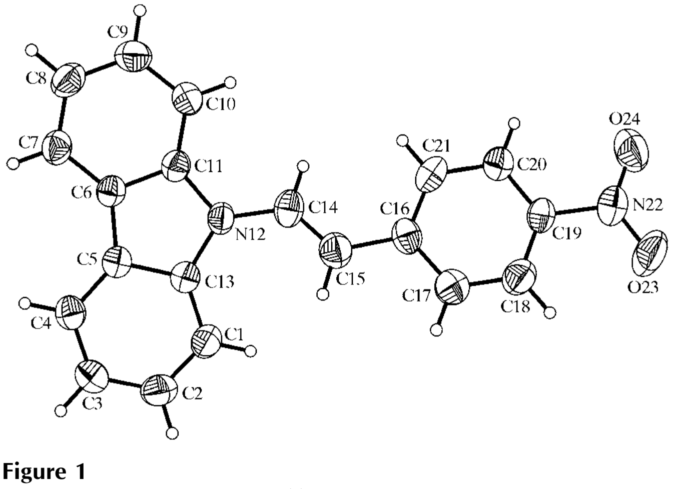


**Figure 1**
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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maximum deviation from the mean plane through all 13 atoms of the carbazole fragment is significantly larger in (II) [0.074 (2) Å] than in (I) [0.028 (1) Å].

In the crystal structures of (I) and (II), van der Waals forces and $\pi$–$\pi$ stacking interactions between the benzene and carbazole moieties seem to be the most important factors determining the packing. In (I), the mean distance between the benzene and carbazole planes, which create a stair-like structure along [001] (Fig. 3), is *ca* 3.45 Å, and the planes are inclined at an angle of 17.1°. In (II), the structure is more complicated. There are two kinds of centrosymmetric dimers, one of stacked molecules, with a mean distance between the planes of 3.30 Å, and the other formed by a number of weak C—H$\cdots$O contacts (Table 3 and Fig. 4). These dimers lie on different centres of symmetry and together also create a stair-like structure (Fig. 5).

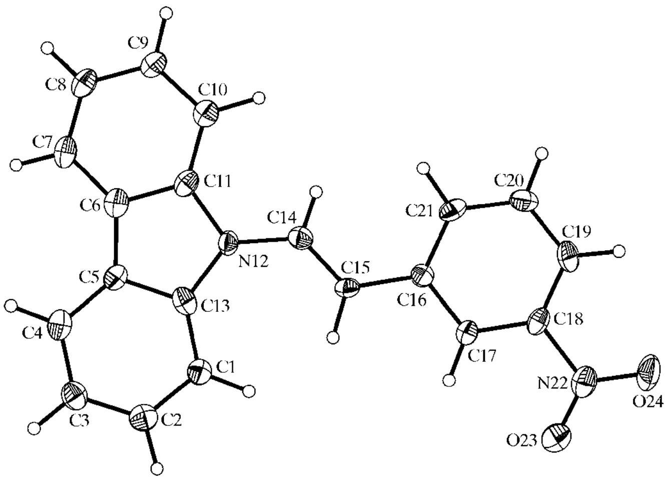

**Figure 2**
A view of the molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

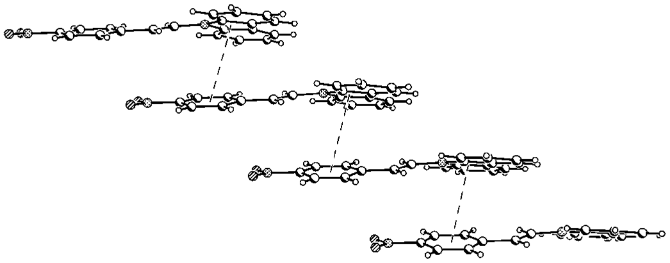

**Figure 3**
The stack of molecules in the structure of (I). The short contacts between the centres of the planar fragments (see *Comment*) are depicted as dashed lines.

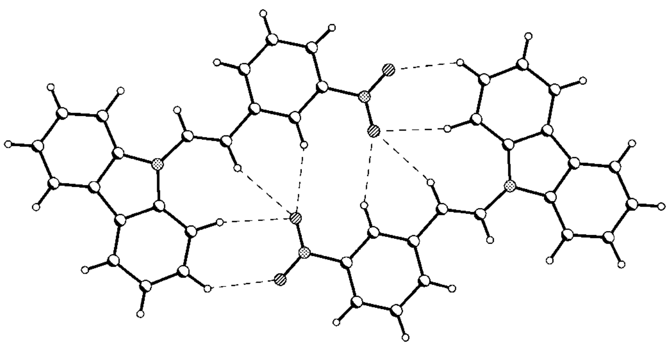

**Figure 4**
C—H$\cdots$O contacts in the centrosymmetric dimer structure of (II). Hydrogen bonds are depicted as dashed lines.

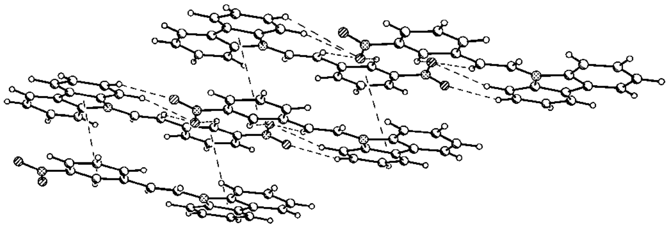

**Figure 5**
The intermolecular interactions (dashed lines) in the structure of (II).

## Experimental

The syntheses of the title compounds have been described elsewhere (Prukała *et al.*, 2007). Crystals appropriate for X-ray diffraction experiments were obtained by slow evaporation from methanol solutions.

### Compound (I)

*Crystal data*

$C_{20}H_{14}N_2O_2$
$M_r$ = 314.33
Monoclinic, $P2_1/n$
$a$ = 6.2627 (9) Å
$b$ = 8.6572 (8) Å
$c$ = 27.943 (2) Å
$\beta$ = 92.578 (10)°
$V$ = 1513.5 (3) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.09 mm$^{-1}$
$T$ = 295 (1) K
0.35 × 0.2 × 0.15 mm

*Data collection*

Kuma KM-4 CCD area-detector diffractometer
12049 measured reflections
3634 independent reflections
1873 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.027

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.106
$S$ = 1.01
3634 reflections
231 parameters
8 restraints
Only H-atom $U$ values refined
$\Delta\rho_{\rm max}$ = 0.31 e Å$^{-3}$
$\Delta\rho_{\rm min}$ = −0.24 e Å$^{-3}$

### Compound (II)

*Crystal data*

$C_{20}H_{14}N_2O_2$
$M_r$ = 314.33
Monoclinic, $P2_1/c$
$a$ = 8.1085 (16) Å
$b$ = 7.5179 (11) Å
$c$ = 24.122 (4) Å
$\beta$ = 90.507 (14)°
$V$ = 1470.4 (4) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.09 mm$^{-1}$
$T$ = 100 (1) K
0.3 × 0.15 × 0.15 mm

*Data collection*

Kuma KM-4 CCD area-detector diffractometer
10298 measured reflections
2555 independent reflections
1278 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.091$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.092$
$S = 0.99$
2554 reflections
217 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.21$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.32$ e Å$^{-3}$

### Table 1
The influence of the substituents on the endocyclic bond angles (°) in the benzene ring of compounds (I) and (II).

Calculated values are taken from Domenicano (1988).

| | (I) (experimental) | (I) (calculated) | (II) (experimental) | (II) (calculated) |
|---|---|---|---|---|
| C21—C16—C17 | 118.2 (2) | 118.7 | 117.1 (2) | 118.5 |
| C16—C17—C18 | 121.5 (2) | 121.2 | 119.0 (3) | 118.9 |
| C17—C18—C19 | 119.5 (2) | 118.4 | 123.8 (3) | 123.2 |
| C18—C19—C20 | 121.7 (2) | 122.5 | 116.9 (2) | 117.7 |
| C19—C20—C21 | 118.4 (2) | 118.4 | 121.2 (3) | 120.6 |
| C20—C21—C16 | 120.7 (2) | 121.2 | 121.9 (3) | 121.2 |

### Table 2
Selected torsion angles (°) and the angles between the mean planes of the planar fragments (°).

*A* is the plane of the carbazole ring system, *B* is the plane of the benzene ring and *C* is the plane of the N—C═C—C bridge; s.u values are given in parentheses.

| | (I) | (II) |
|---|---|---|
| C13—N12—C14—C15 | −10.4 (3) | −4.0 (5) |
| N12—C14—C15—C16 | 178.8 (1) | −179.6 (2) |
| C14—C15—C16—C17 | 179.1 (2) | −175.5 (3) |
| *A*/*B* | 17.91 (6) | 1.71 (10) |
| *A*/*C* | 17.43 (16) | 3.3 (3) |
| *B*/*C* | 1.92 (15) | 5.0 (4) |
| *B*/NO$_2$ | 5.6 (3) | 8.3 (3) |

### Table 3
Hydrogen-bond and short-contact geometry (Å, °) for (II).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| C1—H1$\cdots$O23$^{\rm i}$ | 1.03 | 2.65 | 3.619 (3) | 157 |
| C2—H2$\cdots$O24$^{\rm i}$ | 1.01 | 2.48 | 3.302 (3) | 138 |
| C15—H15$\cdots$O23$^{\rm i}$ | 0.99 | 2.67 | 3.580 (3) | 153 |
| C17—H17$\cdots$O23$^{\rm i}$ | 0.99 | 2.65 | 3.512 (3) | 146 |

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

The positions of the H atoms were found in difference Fourier maps, and their positional parameters were then refined. In the case of (I), their isotropic displacement parameters were also refined. After convergence, the positional parameters were kept as a 'riding model' (C—H = 0.95–1.06 Å), while the displacement parameters were fixed at the refined values in (I) and set at $1.2U_{\rm eq}$(parent) in (II). In (I), some weak restraints on the $U^{ij}$ tensor components of selected atoms were applied.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1989); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3059). Services for accessing these data are described at the back of the journal.

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