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Three 9-[(*E*)-2-(4-halogenophenyl)-vinyl]-9*H*-carbazoles

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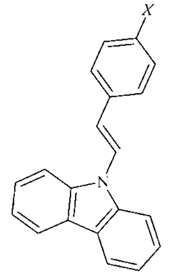
The crystal structures of 9-[(*E*)-2-(4-fluorophenyl)vinyl]-9*H*-carbazole, $C_{20}H_{14}FN$, (I), 9-[(*E*)-2-(4-chlorophenyl)vinyl]-9*H*-carbazole, $C_{20}H_{14}ClN$, (II), and 9-[(*E*)-2-(4-bromophenyl)vinyl]-9*H*-carbazole, $C_{20}H_{14}BrN$, (III), are determined mainly by van der Waals forces. The chloro and bromo derivatives are highly isomorphous, while the fluoro derivative has a different packing mode. Weak C—H···*X* interactions are also involved in the crystal packing. The molecular structures of the three compounds are similar, with relatively large twist angles of *ca* 55° between the carbazole and benzene planes.

Comment

Carbazole and its derivatives have become quite attractive compounds owing to their applications in pharmacy and molecular electronics. Some carbazole alkaloids have been isolated from *Murraya euchrestifolia* (Ito *et al.*, 1991), *Murraya koenigii* (*e.g.* Ito *et al.*, 2006, and references therein) and *Micromelum minutum* (Nakahara *et al.*, 2002). It has been reported that carbazole derivatives possess various biological activities, such as antitumor (Itoigawa *et al.*, 2000), anti-oxidative (Tachibana *et al.*, 2001), anti-inflammatory and antimutagenic (Ramsewak *et al.*, 1999). On the other hand, carbazole and its derivatives are very attractive compounds because of their electroactivity and luminescence properties and are also considered to be potential candidates for electronic devices, such as colour displays, organic semiconductor lasers and solar cells (Friend *et al.*, 1999, and references therein). This molecule with a π-conjugated system is widely used as a good hole-transporting material in polymeric light-emitting diodes (PLEDs) (*e.g.* Zhang *et al.*, 2006) or as an organic light-emitting diode (OLED) (Pan *et al.*, 2005). Carbazole derivatives with *N*-halogenostyryl substituents have important applications in photochemistry, possess an extended π-conjugated double-bond system and can easy undergo further modification (Prukała *et al.*, 2007).



(I) *X*=F
(II) *X*=Cl
(III) *X*=Br

We report here the crystal and molecular structures of three *N*-(halogenostyryl)carbazoles: 9-[(*E*)-2-(4-fluorophenyl)vinyl]-9*H*-carbazole, (I), 9-[(*E*)-2-(4-chlorophenyl)vinyl]-9*H*-carbazole, (II), and 9-[(*E*)-2-(4-bromophenyl)vinyl]-9*H*-carbazole, (III). Comparison of these structures is interesting also from the point of view of crystal engineering; it has been shown that

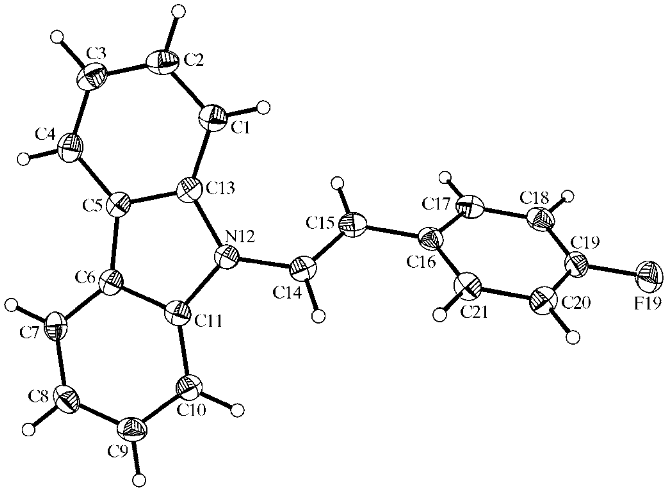


Figure 1
An anisotropic ellipsoid representation of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are depicted as spheres with arbitrary radii.

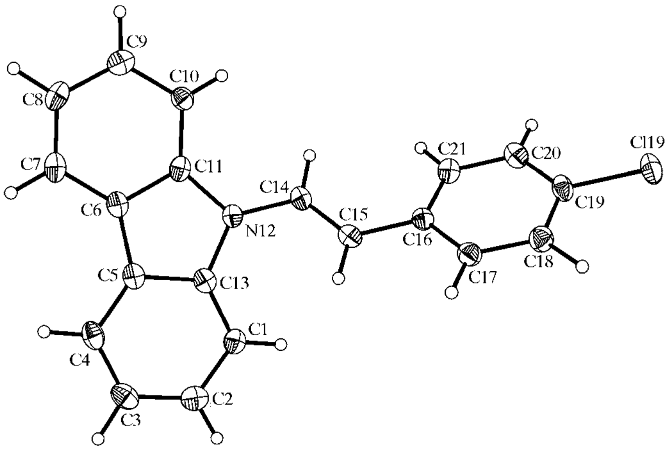


Figure 2
An anisotropic ellipsoid representation of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are depicted as spheres with arbitrary radii.

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in this aspect (intermolecular interactions), fluorine has different properties from the other halogens.

The bond angles within the benzene ring are influenced by the presence of substituents (*cf.* Domenicano, 1988), and the final bond-angle patterns are close to additive combinations of their effects (Table 1); we have observed a similar influence in two nitrovinylcarbazoles (Kubicki *et al.*, 2007).

The conformation of the molecules (Figs. 1 and 2) can be described by the dihedral angles between three approximately planar fragments, *viz*. the carbazole system, the bridging vinyl group and the benzene ring (Table 2). The maximum deviations from the least-squares planes do not exceed 0.070 (2) Å for the carbazole ring system and 0.012 (1) Å for the benzene ring. In contrast to the *m*- and *p*-nitro derivatives (Kubicki *et al.*, 2007), in which these angles are small, in the halogen derivatives the twist is significant, up to almost 60° between the carbazole and benzene ring planes. A similarly large value, 64.29 (4)°, was observed in the structure of 9-[(*E*)-2-(4-methoxyphenyl)vinyl]-9*H*-carbazole (Prukała *et al.*, 2007).

In the crystal structures, van der Waals forces and some weak C—H$\cdots\pi$ and C—H$\cdots X$ interactions (Table 3) seem to be the most important factors determining the packing. Interestingly, contrary to the nitro derivatives, there are no short π–π stacking interactions between the benzene and carbazole ring systems.

The crystal structures of (II) and (III) are highly isomorphous; they crystallize in the same space group, and the unit cells and the packing modes are similar (Fig. 4). To obtain some insight into the degree of isomorphism, we have used the descriptors introduced by Kálmán *et al.* (1991). The unit-cell similarity index, Π, defined as the difference between unity and the ratio of the sums of the orthogonalized unit-cell parameters, is almost ideal (0.01). The isostructurality index, which shows how close are the positions of the atoms in the unit cells, is defined by the sum of the differences between the positions of the analogous atoms. In the case of (II) and (III), the value of this index is also close to the ideal value (99.5%). Kubicki & Szafrański (1998) proposed a modification of this latter parameter, which takes into account the point-group symmetry and gives a more absolute measure of the degree of isostructurality (it should be 1 for ideally isomorphous compounds and 0 for randomly distributed atoms). The value of this modified index is 98.5%.

In all three structures, the crystal packing is determined mainly by van der Waals forces, weak C—H$\cdots\pi$ interactions and some C—H$\cdots X$ interactions. The role of relatively short and directional C—H$\cdots X$ contacts in the crystal packing can be important in the absence of other stronger interactions (*cf.* Desiraju & Steiner, 1999). In isomorphous (II) and (III), C—H$\cdots$Cl and C—H$\cdots$Br hydrogen bonds (Table 3) connect the molecules into infinite chains of 2_1 screw-related molecules along the [010] direction.

In (I), there are also chains of molecules along [010] (Fig. 5); it can be stressed that the unit-cell *b* parameters are very similar in all three structures. Additionally, in (I), C—H$\cdots$F interactions close centrosymmetric dimers (Table 3; *cf.* Chopra & Guru Row, 2005; Chan *et al.*, 2006). The uniqueness of fluorine among the halogens in crystal engineering has often been stressed (*e.g.* Lommerse *et al.*, 1996; Valerio *et al.*, 2000); the differences in the crystal packing of closely related structures described here are just another proof of this phenomenon.

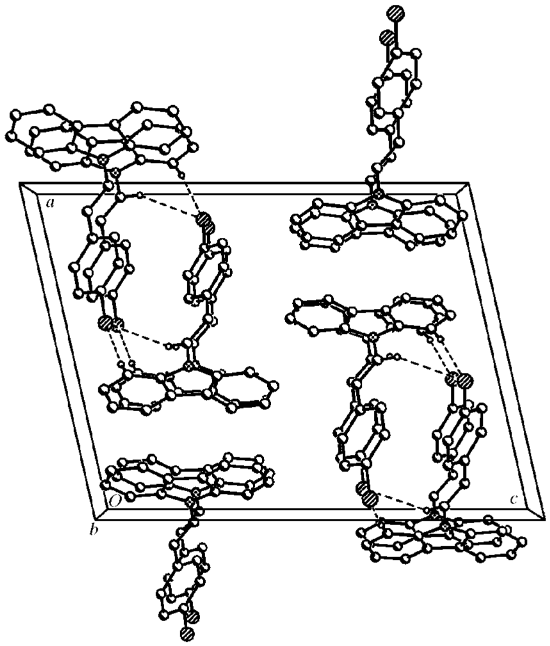

Figure 3
The crystal packing of (II), viewed along the *b* axis. The C—H$\cdots X$ contacts are depicted as dashed lines.

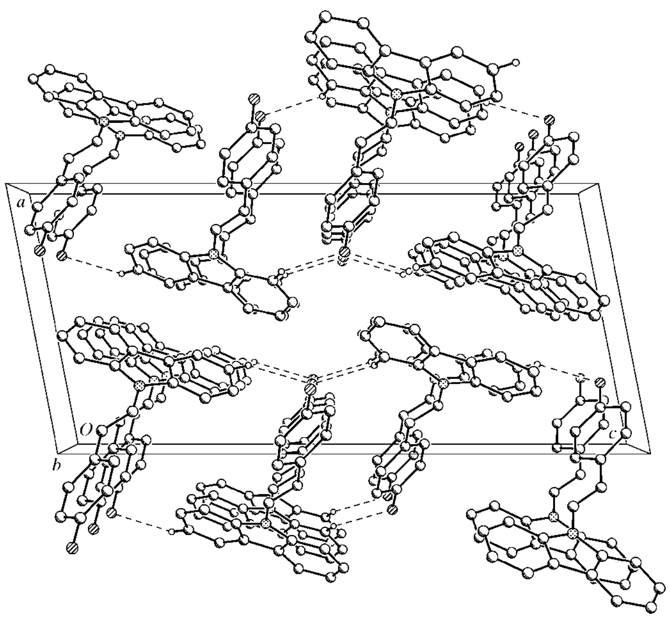

Figure 4
The crystal packing of (I), viewed along the *b* axis.

Experimental

The syntheses of the title compounds are described elsewhere (Prukała *et al.*, 2007). Crystals suitable for X-ray analysis were obtained by slow evaporation from methanol solutions.

Compound (I)

Crystal data

$C_{20}H_{14}FN$
$M_r = 287.32$
Monoclinic, $P2_1/c$
$a = 10.6715$ (5) Å
$b = 5.9502$ (3) Å
$c = 22.9870$ (11) Å
$\beta = 100.953$ (5)°
$V = 1433.03$ (12) 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 four-circle diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{\min} = 0.89$, $T_{\max} = 0.98$
9484 measured reflections
3593 independent reflections
1963 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.060$
$S = 1.01$
3593 reflections
255 parameters
All H-atom parameters refined
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 1
The influence of the substituents on the endocyclic bond angles (°) in the benzene ring.

The 'calc' values are taken from Domenicano (1988) and (for Br) from a Cambridge Structural Database (Allen, 2002) analysis.

Angle	(I)-exp	(I)-calc	(II)-exp	(II)-calc	(III)-exp	(III)-calc
C21—C16—C17	117.8 (1)	117.8	117.8 (1)	118.0	117.7 (2)	117.9
C16—C17—C18	121.8 (1)	121.3	121.9 (2)	121.4	122.3 (2)	121.4
C17—C18—C19	117.8 (1)	118.3	118.7 (2)	118.9	118.3 (2)	119.3
C18—C19—C20	123.2 (1)	123.0	121.2 (1)	121.5	121.5 (2)	120.7
C19—C20—C21	118.2 (1)	118.3	119.4 (2)	118.9	119.5 (2)	119.3
C20—C21—C16	121.2 (1)	121.3	121.0 (2)	121.4	120.8 (2)	121.4

Compound (II)

Crystal data

$C_{20}H_{14}ClN$
$M_r = 303.77$
Monoclinic, $P2_1/n$
$a = 14.3190$ (11) Å
$b = 5.6943$ (5) Å
$c = 18.6247$ (18) Å
$\beta = 102.730$ (7)°
$V = 1481.3$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.25$ mm^{-1}
$T = 100$ (1) K
0.45 × 0.15 × 0.08 mm

Data collection

Kuma KM-4 CCD four-circle diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{\min} = 0.85$, $T_{\max} = 0.98$
12780 measured reflections
3382 independent reflections
2241 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.080$
$S = 1.02$
3382 reflections
241 parameters
Only H-atom coordinates refined
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.29$ e Å^{-3}

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

A is the carbazole ring system, *B* is the benzene ring and *C* is the N—C═C—C bridge.

	(I)	(II)	(III)
C13—N12—C14—C15	−26.8 (2)	−24.4 (2)	−23.8 (3)
N12—C14—C15—C16	−177.6 (1)	−178.6 (1)	−178.4 (2)
C14—C15—C16—C17	156.8 (1)	160.7 (1)	162.3 (2)
A/*B*	58.28 (3)	53.57 (4)	54.04 (6)
A/*C*	36.36 (9)	35.46 (8)	34.62 (10)
B/*C*	22.22 (13)	18.5 (2)	16.9 (3)

Compound (III)

Crystal data

$C_{20}H_{14}BrN$
$M_r = 348.23$
Monoclinic, $P2_1/n$
$a = 14.5152$ (5) Å
$b = 5.6485$ (2) Å
$c = 18.8260$ (6) Å
$\beta = 103.605$ (3)°
$V = 1500.22$ (9) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.74$ mm^{-1}
$T = 100$ (1) K
0.3 × 0.12 × 0.1 mm

Data collection

Kuma KM-4 CCD four-circle diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{\min} = 0.44$, $T_{\max} = 0.77$
9787 measured reflections
3714 independent reflections
2839 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.066$
$S = 1.08$
3714 reflections
199 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.56$ e Å^{-3}
$\Delta\rho_{\min} = -0.57$ e Å^{-3}

Table 3
Hydrogen-bond and short-contact data (Å, °).

*Cg*3 and *Cg*4 denote the centroids of the C6–C11 and C16–C21 rings.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
Compound (I)				
C1—H1···F19$^{\rm i}$	0.974 (11)	2.597 (10)	3.2788 (14)	127.2 (8)
C8—H8···F19$^{\rm ii}$	0.974 (11)	2.608 (11)	3.3970 (15)	138.2 (9)
C4—H4···*Cg*3$^{\rm iii}$	0.958 (11)	2.839 (16)	3.671 (12)	145.8 (9)
C9—H9···*Cg*4$^{\rm iv}$	0.954 (12)	2.834 (16)	3.698 (11)	151.0 (9)
Compound (II)				
C10—H10···Cl19$^{\rm v}$	0.916 (16)	2.879 (16)	3.7871 (16)	171.1 (12)
C14—H14···Cl19$^{\rm v}$	0.985 (15)	2.995 (15)	3.8644 (17)	147.9 (11)
C4—H4···*Cg*3$^{\rm vi}$	0.952 (16)	2.870 (16)	3.624 (2)	136.9 (12)
Compound (III)				
C10—H10···Br19$^{\rm v}$	0.95	2.93	3.8738 (19)	174
C14—H14···Br19$^{\rm v}$	0.95	3.15	4.0036 (19)	150
C4—H4···*Cg*3$^{\rm vi}$	0.95	2.86	3.621 (3)	138

Symmetry codes: (i) $-x, -y-1, -z+1$; (ii) $-x, y+\frac{3}{2}, -z+\frac{3}{2}$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$; (v) $-x-\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (vi) $x, y-1, z$.

The positions of H atoms in the structures of (I) and (II) were found in difference Fourier maps, and their positional and, in the case of (I), isotropic displacement parameters were refined. For (III), H atoms were placed in ideal positions and refined as riding. The displacement parameters were set at $1.2U_{\rm eq}$ of the carrier atoms in (II) and (III).

For all 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*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3120). Services for accessing these data are described at the back of the journal.

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