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2′-(4-Chlorophenyl)-2,3,4,5,6,7-hexahydro-4′,7′-methanospiro[9*H*-fluorene-9,3′-1*H*-indazole]-1′-carbonitrile and methyl 4′-chloro-2′-(4-chlorophenyl)-1′-cyanospiro[9*H*-fluorene-9,3′-pyrazolidine]-4′-carboxylate

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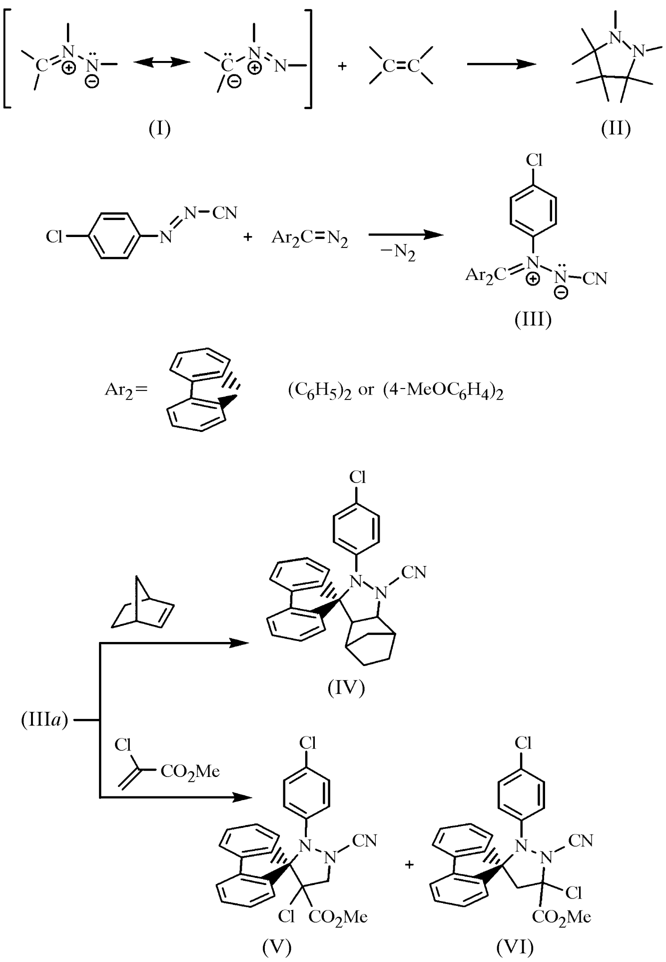
The title compounds, $C_{27}H_{22}ClN_3$, (IV), and $C_{24}H_{17}Cl_2N_3O_2$, (V), were synthesized as part of our ongoing studies on (2+3)-cycloaddition reactions. Compound (V) crystallizes with two molecules in the asymmetric unit. The pyrazolidine ring of compound (IV) adopts a twisted conformation, while in compound (V) it adopts a twisted and an envelope conformation in the two molecules. There are short intermolecular contacts, which can be recognized as unconventional hydrogen bonds, in both structures.

Comment

Azomethine imines, (I), belong to the class of well known and widely applied 1,3-dipoles (Grashey, 1984). They undergo (2+3)-cycloadditions with both electron-rich and electron-deficient ethylene derivatives to yield the corresponding 1,2-pyrazolidine derivatives of type (II). *N*-Cyano-substituted pyrazolidines are of interest because of their expected biological activity; for example, some of them were tested as cathepsin K inhibitors for the treatment of osteoporosis (Deaton *et al.*, 2005). The mechanism of the (2+3)-cycloaddition in the case of azomethine imines is believed to follow the concerted pathway that results in stereospecific formation of the final cycloadducts (Huisgen & Eckell, 1977*a*). For the purposes of organic synthesis, an especially attractive group of 1,3-dipoles is formed by relatively stable and reactive azomethine imines of type (III) prepared from 4-chlorophenyldiazocyanide and diaryl derivatives of diazomethane, described for the first time by Huisgen *et al.* (1977). The yellow crystalline *C*-(2,2′-biphenylylene)-N^{α}-(4-chlorophenyl)-N^{β}-cyanoazomethine imine, (III), reacts smoothly with norbornene and methyl α-chloroacrylate to afford the expected (2+3)-cycloadducts (IV) and (V), respectively, in high yields. The streochemical structures of the isolated products were initially established by Huisgen and co-workers on the basis of the spectroscopic data (Huisgen *et al.*, 1977; Huisgen & Eckell, 1977*b*). The (2+3)-cycloaddition with norbornene was reported to give the *exo*-oriented cycloadduct (Huisgen & Eckell, 1977*a*). In the case of the product obtained from methyl α-chloroacrylate, the reaction was reported to lead mainly to the sterically more crowded regioisomer (V); the minor product corresponding to the structure (VI) was found in the mother liquor after separation of (V) (Huisgen & Eckell, 1977*b*). The goal of the present work was to resynthesize pyrazolidines (IV) and (V), and to confirm their structures and the predicted substitution pattern in the pyrazolidine ring by X-ray diffraction analysis. Other features related to the intermolecular interactions were also of interest.



Compound (IV) (Fig. 1) crystallizes with one molecule and compound (V) (Fig. 2) with two independent molecules in the asymmetric unit [(V-*A*) and (V-*B*)]. The weighted r.m.s. fit of the non-H atoms from the two molecules of (V) is 2.88 Å (Mackay, 1984). The largest deviation from perfect overlap is observed for the fluorene group. The molecules of both compounds contain the pyrazolidine ring as a relevant frag-

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ment of the structure. The substituents at atoms C3, N1 and N2 in both compounds are identical, as they originate from the same 1,3-dipole, (III*a*). In the molecule of (IV), the norbornane ring is fused with the heterocyclic ring, and in the case of (V), the Cl atom and ester group are bonded to atom C4. Thus, the regiochemical structure attributed to (V) by Huisgen & Eckell (1977*a*) was correct. Moreover, the structure of (IV) shows that the pyrazolidine ring is *exo*-oriented with respect to the norbornane skeleton. It is worth mentioning that an analogous orientation was proposed for (2+3)-cycloadducts obtained from norbornene and other 1,3-dipoles, for example, diphenylnitrilimine, benzonitrile *N*-oxide (Huisgen *et al.*, 1967) and methyl diazoacetate (Gorpinchenko *et al.*, 2006).

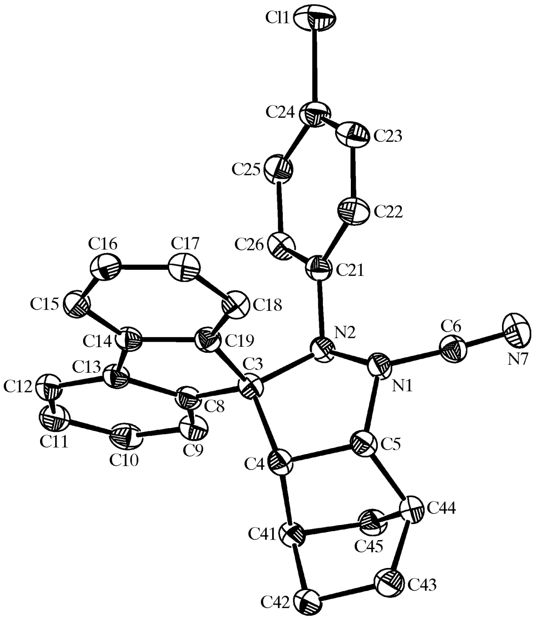


Figure 1
The molecular structure of (IV), showing the atomic numbering scheme and 40% probability displacement ellipsoids. H atoms have been omitted for clarity.

The sums of the bond angles around atom N1 [atom N101 in (V-*B*)] are 343 (1), 336 (1) and 336 (1)° for (IV), (V-*A*) and (V-*B*), respectively, while the corresponding angle sums around atom N2 [atom N102 in (V-*B*)] are 324 (1), 342 (1) and 343 (1)°, respectively. These values indicate significant pyramidalization at these N atoms. A similar pyramidalization about the cyano N atom is found in other heterocyclic compounds containing the –N—C≡N group (Bird *et al.*, 1995). In contrast, the amine N atom of the parent cyanamide, CH_2N_2, has a geometry that is somewhat flatter; the sums of the bond angles were found to be 356 (2)° in a low-temperature X-ray study (Denner *et al.*, 1988), and 349.3 (7) and 349.6 (7)° in a study based on neutron data and an X-ray multipole refinement, respectively, for a host–guest complex of cyanamide in 18-crown-6 (Koritsanszky *et al.*, 1991).

The pyrazolidine ring in each compound is nonplanar, as the three C atoms and two N atoms are sp^3-hybridized. In (IV), this ring adopts a twisted conformation, with the pseudo-twofold axis passing through the mid-point of the N2—C3 bond and atom C5. For (IV), the puckering parameters (Cremer & Pople, 1975) for the atom sequence N1—N2—C3—C4—C5 are q_2 = 0.385 (1) Å and φ_2 = 229.8 (2)° [asymmetry parameter (Nardelli, 1983) Δ_2 = 0.019 (1)]. The substituents at atoms N1 and N2 occupy equatorial positions, while atoms C41 and C44 are in axial positions with respect to the pyrazolidine ring. The pyrazolidine ring of (V) adopts an envelope conformation in molecule *A*, with a pseudo-mirror passing through atom C4 and the mid-point of the N1—N2 bond. In molecule *B*, the ring has a twisted conformation, with

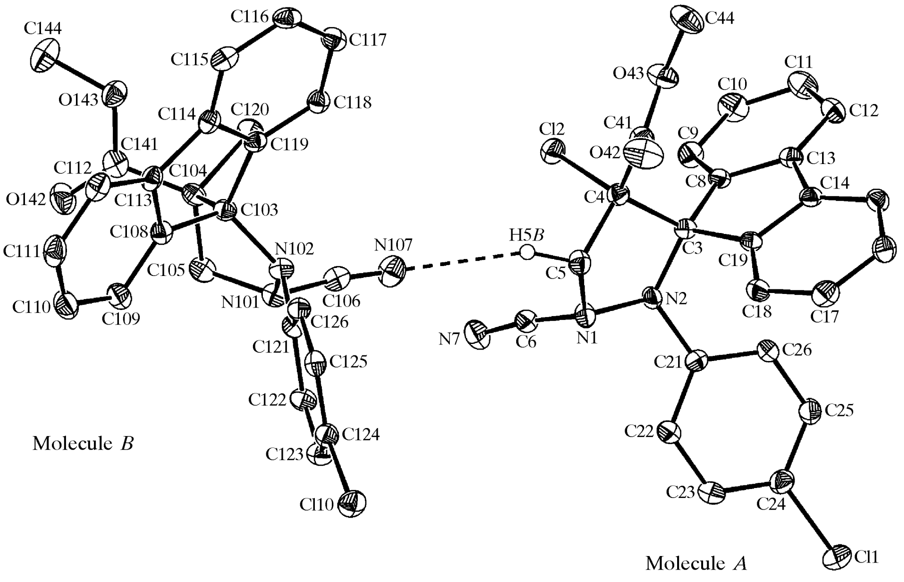
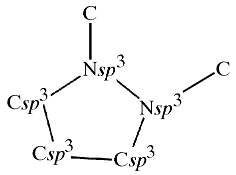


Figure 2
The molecular structures of the two symmetry-independent molecules of (V), showing the atomic numbering schemes and 40% probability displacement ellipsoids. The C—H···N interaction forming dimers between molecules *A* and *B* is shown as a dashed line. The other H atoms have been omitted for clarity.

the pseudo-twofold axis passing through the mid-point of the C104—C105 bond and atom N102. For (V-*A*), the puckering parameters for the atom sequence N1—N2—C3—C4—C5 are q_2 = 0.400 (2) Å and φ_2 = 295.1 (3)° [asymmetry parameter Δ_s = 0.041 (1)], while for (V-*B*) the puckering parameters for the atom sequence N101—N102—C103—C104—C105 are q_2 = 0.389 (2) Å and φ_2 = 128.4 (3)° [Δ_2 = 0.013 (1)]. The different puckering of the pyrazolidine rings of molecules *A* and *B* causes differences in the orientations of the substituents. The cyano group at atom N1 is nearly axial and perfectly axial at atom N101. In both molecules of compound (V), the chlorophenyl substituent at atom N2 (N102) occupies a nearly equatorial position, while the Cl and ester substituents at atom C4 (C104) occupy axial and equatorial positions, respectively.

The bonds distances and angles in all three molecules are mostly in good agreement with expected values (Allen *et al.*, 1987). However, the N—N bond distances are longer than expected. The long N1—N2 bond of 1.4785 (15) Å in (IV) and 1.458 (3) and 1.445 (3) Å in (V-*A*) and (*V-B*), respectively, may be caused by the influence of the cyano and chlorophenyl substituents on the pyrazolidine ring. Moreover, a search of the Cambridge Structural Database (Version 5.28 of November 2006; Allen, 2002) for structures containing the pyrazolidine fragment (see scheme below), revealed a range of N—N bond lengths from 1.387 to 1.514 Å for 42 structures. The search was limited to ordered structures, without errors, with *R* less than 0.05 and an average bond length s.u. smaller than 0.005 Å.

In (IV), atom N7^i [symmetry code: (i) $x - 1, y, z$] is involved in an unconventional C17—H17···N7^i hydrogen bond, which links the molecules into chains along the [100] direction (Fig. 3). This generates a graph-set motif of *C*(9) (Etter *et al.*, 1990). In contrast, molecules *A* and *B* in (V) are linked into dimers by a weak C5—H5*B*···N107 interaction; atom N7 does not act as an acceptor in any interaction. In addition, some weak nonclassical intermolecular C—H···O, C—H···Cl and C—H···π interactions are observed. For (IV), a C—H···π interaction (see Table 1, where *Cg*1 is the centroid of the C8–C13 ring of the fluorene group) involves pairs of molecules related by a centre of inversion. For (V) (see Table 2, where *Cg*2 is the centroid of the C121–C126 ring of molecule *B*), all interactions emanate from H atoms solely in molecule *A* and the acceptor atoms are in one adjacent molecule *A* and three different *B* molecules.



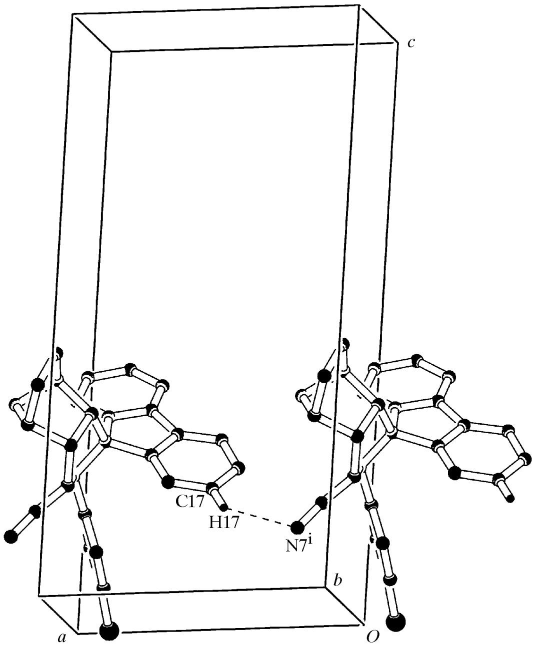


Figure 3
Part of the crystal structure of (IV), showing the C—H···N interaction forming chains along the *a* axis. The symmetry code is given in Table 1.

Experimental

Compound (III) was prepared following a literature protocol (Huisgen *et al.*, 1977); compounds (IV) and (V) were synthesized from (III) and commercial norbornene or methyl α-chloroarylate, according to the procedures reported by Huisgen & Eckell (1977*a*) and Huisgen & Eckell (1977*b*), respectively. Crystals suitable for X-ray measurement were obtained by slow evaporation from a dichloromethane/methanol (1:3) mixture. The melting points are 458–459 K for (IV) and 454–455 K for (V) [the previously reported melting points were 461–462 K for (IV) (Huisgen & Eckell, 1977*a*) and 456–457 K for (V) (Huisgen & Eckell, 1977*b*)].

Compound (IV)

Crystal data

$C_{27}H_{22}ClN_3$
M_r = 423.93
Monoclinic, $P2_1/n$
a = 9.0914 (9) Å
b = 12.6225 (9) Å
c = 18.5025 (17) Å
β = 94.576 (8)°
V = 2116.5 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.20 mm^{-1}
T = 173 (2) K
0.35 × 0.15 × 0.10 mm

Data collection

Stoe IPDSII image-plate diffractometer
17870 measured reflections
5071 independent reflections
3437 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.081
S = 0.85
5071 reflections
280 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.24 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.30 e Å^{-3}

Table 1
Short-contact geometry (Å, °) for (IV).

*Cg*1 is the centroid of the C8–C13 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C17—H17···N7^i	0.93	2.65	3.418 (1)	141
C42—H42*B*···*Cg*1^{ii}	0.97	2.74	3.484 (2)	134

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 2, -y + 1, -z + 1$.

Compound (V)

Crystal data

$C_{24}H_{17}Cl_2N_3O_2$
$M_r = 450.31$
Monoclinic, $P2_1/c$
$a = 11.1818\ (5)$ Å
$b = 13.2534\ (4)$ Å
$c = 28.1265\ (11)$ Å
$\beta = 96.363\ (3)^\circ$
$V = 4142.6\ (3)$ Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.34$ mm^{-1}
$T = 120\ (2)$ K
0.37 × 0.37 × 0.08 mm

Data collection

Stoe IPDSII image-plate diffractometer
23396 measured reflections
7295 independent reflections
4866 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.079$
$S = 1.02$
7295 reflections
559 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max} = 0.84$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.41$ e Å^{-3}

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

*Cg*2 is the centroid of the C121–C126 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5*B*···N107	0.99	2.51	3.459 (3)	160
C23—H23···O142^{i}	0.95	2.57	3.502 (3)	166
C25—H25···*Cg*2^{ii}	0.95	2.50	3.400 (2)	158
C44—H44*A*···Cl1^{iii}	0.98	2.77	3.425 (3)	125

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

All H atoms were positioned geometrically and refined using a riding model. In (IV), $U_{\rm iso}$(H) values were constrained to $1.2U_{\rm eq}$(C), with C—H distances of 0.98, 0.97 and 0.93 Å for methine, methylene and aromatic groups, respectively. In (V), for methyl H atoms, $U_{\rm iso}$(H) values were constrained to $1.5U_{\rm eq}$(C), with C—H distances of 0.98 Å; the C—H distances are 0.95 and 0.99 Å for the aromatic and methylene groups, respectively, with $U_{\rm iso}$(H) values constrained to $1.2U_{\rm eq}$(C).

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2000); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3061). Services for accessing these data are described at the back of the journal.

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