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Three polar derivatives of *N*-ethylcarbazole: materials for optical applications

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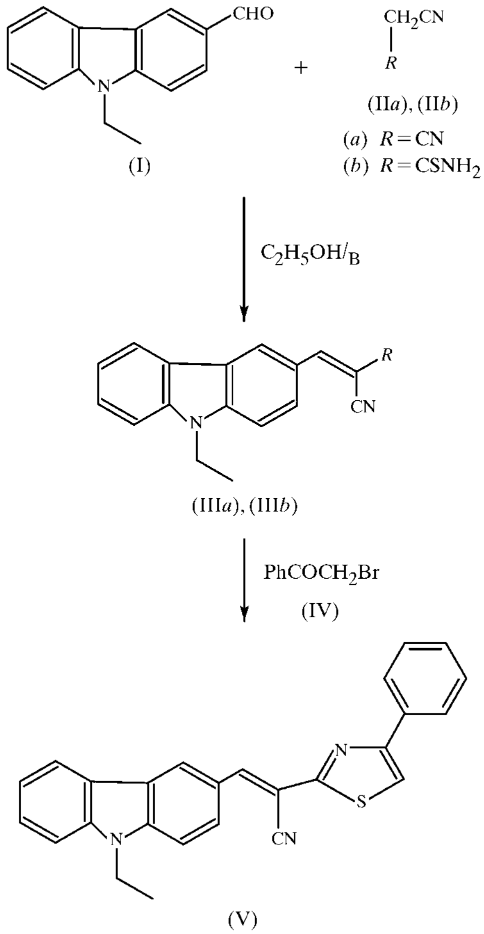
Three *N*-ethylcarbazole derivatives have been synthesized and tested for non-linear optical (NLO) properties. The compounds are 2-(9-ethyl-9*H*-carbazol-3-ylmethylene)-malononitrile, $C_{18}H_{13}N_3$, (III*a*), 2-cyano-3-(9-ethyl-9*H*-carbazol-3-yl)thioacrylamide, $C_{18}H_{15}N_3S$, (III*b*), and 3-(9-ethyl-9*H*-carbazol-3-yl)-2-(4-phenyl-1,3-thiazol-2-yl)acrylonitrile, $C_{26}H_{19}N_3S$, (V). It was found that the molecules of (III*a*) and (V) are nearly planar, while non-planarity is more pronounced for (III*b*). Molecules of (III*a*) and (V) exhibit herring-bone packing motifs. In (III*b*), the molecules form layers coplanar with ($\bar{2}01$), within which they form centrosymmetric dimers *via* N—H···S hydrogen bonds.

Comment

Polar organic molecules as components of NLO, electro-optical, photorefractive and optical-limiting materials have been under intensive investigation for the last two decades (*e.g.* Zyss, 1994; Nalwa & Miyata, 1997; Kuzyk & Dirk, 1998). Structural data, along with theoretical calculations and experimental measurements, help to reveal the nature of the relevant structure–property relationships. The present investigation is a continuation of our project which incorporates the synthesis, structural studies and evaluation of properties of organic compounds for potential optical applications (Antipin *et al.*, 1997, 1998, 2001; Timofeeva *et al.*, 2000; Nesterov *et al.*, 2000). To our knowledge, no structural information on NLO carbazole derivatives has previously been available. Recently, we have synthesized and characterized a series of *N*-ethylcarbazole derivatives, *i.e.* (III*a*), (III*b*) and (V), shown in the synthetic scheme below.

In this paper, we present the results of structural investigations and the evaluation of second-harmonic generation (SHG) in solution for compounds (III*a*), (III*b*) and (V). Recently, we investigated another polar *N*-ethylcarbazole derivative, namely (*E*)-4-(9-ethyl-9*H*-carbazol-3-ylvinyl)-*N*-methylpyridinium iodide, (VI) (Wang *et al.*, 2001), and we will compare the molecular geometry parameters for all four of these compounds.



The polar molecules under investigation can be formally divided into three planar fragments: a donor part, *D*, comprising the *N*-ethylcarbazole moiety less the ethyl group, a bridging part, *B* [–CH=C< in (III*a*), (III*b*) and (V), but –CH=CH– in (VI)], and an acceptor part, *A*, which differs in each molecule. The geometric parameters for *N*-ethylcarbazole in (III*a*), (III*b*) and (V), and in the two crystallographically independent molecules of (VI) are very similar and do not vary from the standard values for the corresponding heterocyclic systems (Allen *et al.*, 1987). The orientation of the *N*-ethyl substituents in all the molecules is almost perpendicular to the carbazole plane (Tables 1, 2 and 4). In all the molecules, the bridging part *B* has a C=C bond which is slightly longer than the standard value (Allen *et al.*, 1987). As the attached single bonds are slightly shorter (Tables 1, 2 and 4), this is evidence of some delocalization in the bridging units of these molecules.

The geometric parameters of the dicyanovinyl acceptor fragment in molecule (III*a*) (Fig. 1) are standard (Timofeeva *et al.*, 2000). The molecule of (III*a*) is almost planar, the dihedral angle between the least-squares mean planes of the donor part *D* and the dicyanovinyl group being 5.1 (1)°. This does not differ significantly from the results for other dicyanovinylaryl

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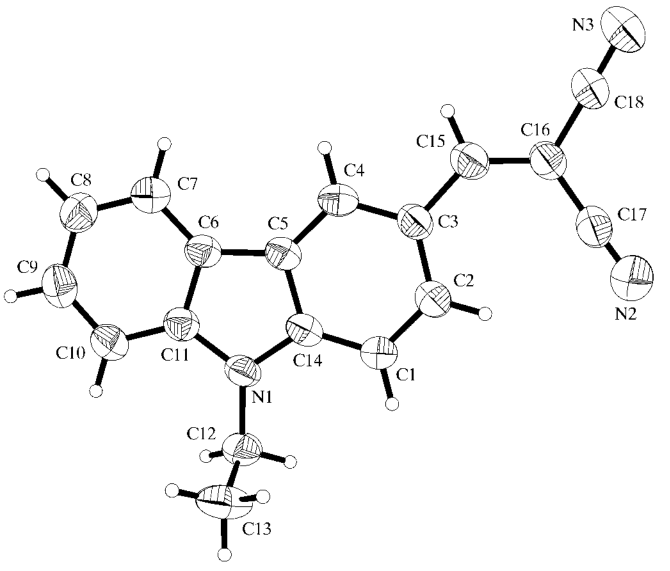

Figure 1

A view of the molecule of (III*a*) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

molecules (Timofeeva *et al.*, 2000). Molecules of (III*a*) adopt a herring-bone packing motif.

The Cambridge Structural Database (CSD, April 2001 release; Allen & Kennard, 1993) contains only one compound, namely *trans,trans*-2-cyano-5-(4-methoxyphenyl)penta-2,4-dienethioamide (Nesterov *et al.*, 2000), which has mutually *trans* CN and S substituents and is suitable for direct comparison with the cyanovinylthioamide fragment found in (III*b*) (Fig. 2). In the other two known structures containing such fragments, the cyano and thio substituents are mutually *cis* (Brunskill *et al.*, 1984; Nesterov *et al.*, 1991). The different relative orientations of the substituents do not significantly influence the bond lengths and angles in this fragment, and their values are very similar in all these molecules.

The molecule of (III*b*) is less planar than that of (III*a*); the dihedral angle between the *D* and *B* fragments is 15.5 (1)°, and between *B* and *A* it is 12.0 (2)°. The molecules pack in layers coplanar with $(\bar{2}01)$. Within these layers, (III*b*) forms centrosymmetric dimers *via* N3—H3*B*···S1^{i} hydrogen bonds [Table 3; symmetry code: (i) $1 - x, 1 - y, 2 - z$].

In molecule (V) (Fig. 3), the values for the molecular geometry parameters of the phenylthiazole (Ph–T) substituents are similar to those of the other examples found in the CSD. The dihedral angles between the planar fragments in (V) are *D*/*B* 6.3 (1), *B*/T 5.0 (1) and T/Ph 4.2 (1)°. The molecule of (V) has a mutually *transoid* orientation of the S1 atom and C15=C16 bridge ('bent' conformation) (Fig. 3). The other possible conformation ('stretched') has a *cisoid* orientation of the S1 atom and double bond. Using molecular mechanics, we compared the relative energies of the 'bent' and 'stretched' molecules of (V). We found that the 'stretched' conformation is favoured (the energy difference is 2.1 kcal mol^{-1}; 1 kcal mol^{-1} = 4.184 kJ mol^{-1}), and this suggests that under other circumstances (*e.g.* in solution or in another polymorph), molecule (V) might adopt a different conformation. Molecules of (V) exhibit a herring-bone pattern in their packing.

All the crystalline samples investigated here are centrosymmetric, so they cannot manifest SHG in their crystalline phases. X-ray powder diffraction has shown that for both (III*b*) and (V), the crystalline phase present in the powder samples and in single crystals is the same. In contrast, the powder diffraction pattern for compound (III*a*) shows the presence of another crystalline phase. Unfortunately, we have not been able to obtain single crystals of the second phase of (III*a*) by conventional methods and we are currently investigating other approaches to growing single crystals suitable for X-ray investigation.

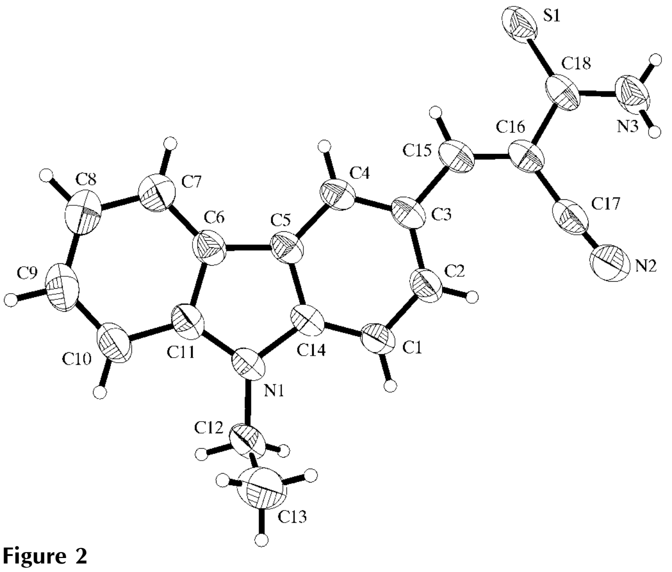

Figure 2

A view of the molecule of (III*b*) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

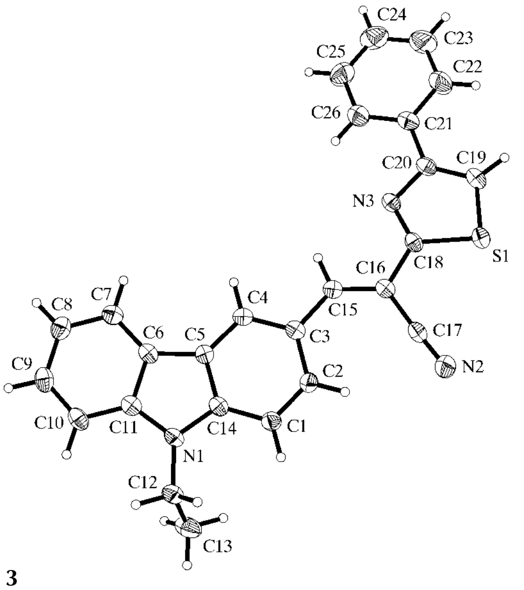

Figure 3

A view of the molecule of (V) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

SHG in solution can be measured after orientation of the molecules by an electric field. Electric field-induced second harmonic generation (EFISH) measurements of hyperpolarizability $\beta(\omega)$ in solution gave values of 42.5, 60.2 and 65.2×10^{-30} esu for molecules (III*a*), (III*b*) and (V), respectively. These results suggest that materials incorporating molecules of (III*b*) or (V) might be as efficient as traditional cyanovinyl derivatives (Antipin *et al.*, 1997), but their melting points and thermal stabilities would both be higher because of the presence of the *N*-ethylcarbazole moiety.

Experimental

Compounds (III*a*) and (III*b*) were obtained by the reaction of *N*-ethyl-3-carbazolealdehyde (1.115 g, 0.005 mol), (I), with malononitrile (0.330 g, 0.005 mol), (II*a*), or 2-cyanothioacetamide (0.500 g, 0.005 mol), (II*b*), respectively, in the presence of a catalytic amount of morpholine in ethanol (20 ml) at room temperature. The precipitates which separated were recrystallized from ethanol (30 ml) and acetonitrile (30 ml), respectively [m.p. 431 K, yield 1.018 g (75%) for (III*a*); m.p. 490 K, yield 1.176 g (77%) for (III*b*)]. Compound (V) was obtained by the reaction of (III*b*) (1.527 g, 0.005 mol) with 2-bromoacetophenone (0.995 g, 0.005 mol), (IV), in dimethylformamide (20 ml) at room temperature. The precipitate which separated was recrystallized from acetonitrile (30 ml) [m.p. 428 K, yield 1.521 g (75%)]. Crystals were obtained by isothermal evaporation from ethanolic solutions of (III*a*) or (III*b*), and from a solution of (V) in acetonitrile.

Compound (III*a*)

Crystal data

$C_{18}H_{13}N_3$
$M_r = 271.31$
Monoclinic, $P2_1/c$
$a = 12.731$ (3) Å
$b = 4.2160$ (8) Å
$c = 26.640$ (5) Å
$\beta = 96.87$ (3)°
$V = 1419.6$ (5) Å^3
$Z = 4$
$D_x = 1.269$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 11$–12°
$\mu = 0.08$ mm^{-1}
$T = 298$ (2) K
Needle, yellow
$0.5 \times 0.1 \times 0.1$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
2575 measured reflections
2458 independent reflections
1280 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 5$
$l = -31 \rightarrow 31$
3 standard reflections every 97 reflections
intensity decay: 3%

Table 1
Selected geometric parameters (Å, °) for (III*a*).

N2—C17	1.142 (4)	C15—C16	1.355 (4)
N3—C18	1.138 (4)	C16—C18	1.424 (5)
C3—C15	1.432 (4)	C16—C17	1.431 (5)
C2—C3—C15	125.1 (3)	C18—C16—C17	115.2 (3)
C16—C15—C3	131.6 (3)	N2—C17—C16	178.3 (4)
C15—C16—C18	119.6 (3)	N3—C18—C16	178.6 (4)
C15—C16—C17	125.2 (3)		
C11—N1—C12—C13	−87.8 (4)		

Table 2
Selected geometric parameters (Å, °) for (III*b*).

S1—C18	1.665 (2)	C15—C16	1.351 (3)
N2—C17	1.146 (3)	C16—C17	1.435 (3)
N3—C18	1.327 (2)	C16—C18	1.488 (2)
C3—C15	1.445 (2)		
C2—C3—C15	123.66 (17)	N2—C17—C16	175.4 (2)
C16—C15—C3	131.64 (18)	N3—C18—C16	115.93 (17)
C15—C16—C17	123.41 (16)	N3—C18—S1	121.89 (14)
C15—C16—C18	121.76 (17)	C16—C18—S1	122.14 (14)
C17—C16—C18	114.82 (16)		
C11—N1—C12—C13	−93.0 (2)		

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.156$
$S = 1.00$
2458 reflections
191 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.062P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}

Compound (III*b*)

Crystal data

$C_{18}H_{15}N_3S$
$M_r = 305.39$
Triclinic, $P\overline{1}$
$a = 8.4370$ (17) Å
$b = 8.7500$ (17) Å
$c = 12.300$ (3) Å
$\alpha = 79.82$ (3)°
$\beta = 76.82$ (3)°
$\gamma = 63.76$ (3)°
$V = 790.0$ (3) Å^3
$Z = 2$
$D_x = 1.284$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 11$–12°
$\mu = 0.20$ mm^{-1}
$T = 298$ (2) K
Parallelepiped prism, orange
$0.50 \times 0.35 \times 0.30$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
2971 measured reflections
2762 independent reflections
2257 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.013$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 10$
$k = -9 \rightarrow 10$
$l = -14 \rightarrow 14$
3 standard reflections every 97 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.114$
$S = 1.05$
2762 reflections
200 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.24P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.33$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

Compound (V)

Crystal data

$C_{26}H_{19}N_3S$
$M_r = 405.50$
Monoclinic, $P2_1/c$
$a = 19.384$ (5) Å
$b = 16.456$ (4) Å
$c = 6.5323$ (17) Å
$\beta = 95.637$ (19)°
$V = 2073.6$ (9) Å^3
$Z = 4$
$D_x = 1.299$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10$–11°
$\mu = 0.17$ mm^{-1}
$T = 155$ (2) K
Parallelepiped prism, yellow
$0.45 \times 0.30 \times 0.25$ mm

Table 3
Hydrogen-bonding geometry (Å, °) for (III*b*).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3$B\cdots$S1$^{\rm i}$	0.86	2.55	3.402 (2)	170

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

Table 4
Selected geometric parameters (Å, °) for (V).

S1—C18	1.7342 (18)	C3—C15	1.448 (2)
S1—C19	1.712 (2)	C15—C16	1.358 (2)
N2—C17	1.146 (2)	C16—C17	1.434 (3)
N3—C18	1.307 (2)	C16—C18	1.471 (2)
N3—C20	1.383 (2)	C19—C20	1.362 (3)
C18—S1—C19	88.93 (9)	N3—C18—C16	123.25 (16)
C18—N3—C20	111.08 (15)	N3—C18—S1	114.59 (13)
C2—C3—C15	124.00 (16)	C16—C18—S1	122.16 (14)
C16—C15—C3	131.52 (17)	C20—C19—S1	111.09 (14)
C15—C16—C17	124.43 (16)	C19—C20—N3	114.30 (17)
C15—C16—C18	120.34 (16)	C19—C20—C21	126.89 (17)
C17—C16—C18	115.21 (16)	N3—C20—C21	118.81 (17)
N2—C17—C16	177.5 (2)		
C11—N1—C12—C13	104.1 (2)	N3—C20—C21—C26	−3.4 (3)
C15—C16—C18—N3	−4.4 (3)		

Data collection

Syntex $P2_1$ diffractometer
$\theta/2\theta$ scans
4942 measured reflections
4540 independent reflections
3066 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\rm max} = 27.1°$
$h = -24 \rightarrow 24$
$k = -21 \rightarrow 1$
$l = 0 \rightarrow 8$
2 standard reflections
every 98 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.112$
$S = 0.92$
4540 reflections
272 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.068P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.30$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.32$ e Å^{-3}

Molecular mechanics calculations were carried out using *MM*3 (Allinger *et al.*, 1989; Lii & Allinger, 1989). EFISH measurements of hyperpolarizability for the three compounds in solution were performed using the methods described by Sanghadasa *et al.* (1996) and Antipin *et al.* (1997). H atoms were placed geometrically; for (III*a*) and (V), those attached to sp^2, methyl and methylene C atoms were set at distances of 0.95, 0.98 and 0.99 Å, respectively. For (III*b*), the corresponding distances were 0.93, 0.96 and 0.97 Å. For methyl H atoms, $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm C})$, and for all other H atoms, $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

For compounds (III*a*) and (III*b*), data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*. For compound (V), data collection: *P*3 (Siemens, 1989); cell refinement: *P*3. For all three compounds, data reduction: *SHELXTL-Plus* (Sheldrick, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1472). Services for accessing these data are described at the back of the journal.

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