Crystal structure of 9-ethyl-3-[(*E*)-2-(thiophen-2-yl)vinyl]-9*H*-carbazole, $C_{20}H_{17}NS$

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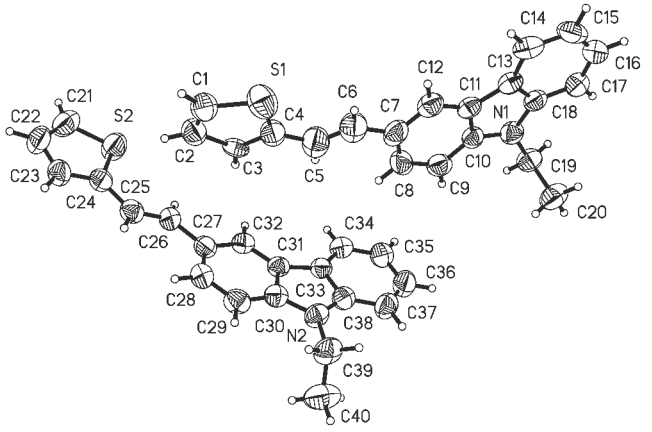

Abstract

$C_{20}H_{17}NS$, monoclinic, $P2_1$ (no. 4), a = 11.8160(2) Å, b = 5.5980(1) Å, c = 24.4572(3) Å, β = 97.619(1)°, V = 1603.5 Å^3, Z = 4, $R_{gf}(F)$ = 0.057, $wR_{ref}(F^2)$ = 0.176, T = 296 K.

Source of material

A mixture of 2-thiophene-triphenylphosphonium bromide (1.8 g, 0.004 mol) and *N*-ethylcarbazole-3-aldehyde (0.89 g, 0.004 mol) was suspended in freshly distilled THF (40 mL) and then potassium *tert*-butoxide (0.67 g, 0.006 mol) in *tert*-butyl alcohol (50 mL) was added dropwise under nitrogen with stirring in an ice bath. The mixture was continuously stirred at room temperature for further 20 h. The mixture was poured into a beaker containing distilled water (200 mL) and the pH value of the mixture was adjusted to 7.0 by addition of dilute hydrochloric acid. This mixture was extracted into dichloromethane and the organic phases were washed twice with distilled water. The organic layer was dried with anhydrous $MgSO_4$ overnight and then the organic solvent was removed using a rotary evaporator. The residue was purified by column chromatography on silica gel using chloroform/petroleum ether (1:8, *v*/*v*) as eluent, and 0.60 g light yellow polycrystals with a yield 49 % were obtained. Needle-like crystals, which were suitable for X-ray crystallography, were obtained by recrystallization from ethanol.

Experimental details

After checking their presence in the difference Fourier map, all H atoms were geometrically fixed and allowed to ride on their attached atoms, with d(C—H) = 0.93 - 0.97 Å and U_{iso}(H) = 1.2 or 1.5 U_{eq}(C). The symmetry was checked by PLATON but no obvious extra crystallographic symmetry was detected.

Discussion

Carbazole derivatives attract considerable research interest in optics and optoelectronics fields due to their perfect planarity and π-conjugation [1,2]. Conjugated bridge can be formed with the nitrogen atom [3] or with phenyl ring in carbazole group [4], so there are two kinds of connections between carbazole group and conjugated bridge. In first connection, the lone electron pair of the nitrogen atom is only delocalized in carbazole group, which limits the intramolecular charge transfer. The second connection is beneficial to molecular conjugation and charge transfer [5]. So in recent molecule design, this connection is often applied.

There are two independent molecules in the asymmetric unit of the title crystal structure. The second molecule exhibits better planarity than the first molecule, which can be indicated by the dihedral angles between the planes of the thiophene group and carbazole group in different molecules. The dihedral angel between thiophene group (S1, C1 to C4) and carbazole group (C7 to C18, N1) in the first molecule is 17.8(2)°, whereas the dihedral angel in the second molecule is 9.6(2)°. These dihedral angels are much smaller than the dihedral angle in a molecule with the nitrogen atom in carbazole group is connected with conjugated bridge. In a such molecule reported, the dihedral angle is usually very large up to 53.95° [6]. The perfect planarity of the backbones of the molecule contributes to the high π-conjugation, which is a necessary condition for non-linear optical effects. The two molecules in one asymmetric unit are nearly perpendicular, with dihedral angles of 76.5(2)° between two thiophene groups and 85.4(1)° between two carbazole groups. The bond lengths of bridging C4—C5=C6—C7 bonds connecting thiophene and carbazole are d(C4—C5) = 1.464(7) Å, d(C5=C6) = 1.268(5) Å, d(C6—C7) = 1.483(7) Å. The bond lengths of C4—C5 and C6—C7 are remarkably shortened compared with typical single C—C bond and the bond length of C5=C6 is remarkably lengthened compared with typical single C=C bond. These data indicate that there is some conjugation between thiophene group and carbazole group along the main axis of the molecular backbone, which can be further proved by the bond lengths of the bridge C24—C25=C26—C27 (d(C24—C25) = 1.448(5) Å, d(C25=C26) = 1.326(6) Å, d(C26—C27) = 1.473(5) Å) in the second molecule.

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Table 1. Data collection and handling.

Crystal:	yellow prism, size 0.17 × 0.20 × 0.27 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.98 cm^{-1}
Diffractometer, scan mode:	Bruker APEX2 CCD, φ/ω
$2\theta_{max}$:	54.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11591, 5555
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4047
$N(param)_{refined}$:	399
Programs:	SIR97 [7], SHELXL-97 [8], SHELXTL [9], WinGX [10], PLATON [11]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	2*a*	0.8986	1.4615	0.1464	0.084
H(2)	2*a*	0.8159	1.1202	0.0993	0.077
H(3)	2*a*	0.7412	0.8214	0.1662	0.052
H(5)	2*a*	0.7299	0.7572	0.2647	0.098
H(6)	2*a*	0.8248	1.1001	0.3324	0.097
H(8)	2*a*	0.6618	0.5578	0.3343	0.080
H(9)	2*a*	0.6389	0.3239	0.4115	0.075
H(12)	2*a*	0.8726	1.0061	0.4261	0.074
H(14)	2*a*	0.9684	1.0415	0.5386	0.078
H(15)	2*a*	1.0101	0.9960	0.6334	0.088
H(16)	2*a*	0.9372	0.6783	0.6771	0.085
H(17)	2*a*	0.8212	0.4029	0.6290	0.078
H(19A)	2*a*	0.7185	0.1408	0.5619	0.072
H(19B)	2*a*	0.6597	0.1229	0.5007	0.072
H(20A)	2*a*	0.5832	0.4218	0.5805	0.121
H(20B)	2*a*	0.5223	0.1854	0.5585	0.121
H(20C)	2*a*	0.5247	0.4061	0.5192	0.121
H(21)	2*a*	0.9867	0.5327	–0.0537	0.100
H(22)	2*a*	0.9029	0.8681	–0.1047	0.098
H(23)	2*a*	0.7344	1.0235	–0.0675	0.078
H(25)	2*a*	0.6087	0.9306	0.0135	0.069
H(26)	2*a*	0.6668	0.5074	0.0642	0.067
H(28)	2*a*	0.4611	0.9749	0.0627	0.070
H(29)	2*a*	0.3333	1.0340	0.1248	0.074
H(32)	2*a*	0.5898	0.3939	0.1445	0.061
H(34)	2*a*	0.5559	0.1567	0.2450	0.075
H(35)	2*a*	0.5010	0.0521	0.3285	0.085
H(36)	2*a*	0.3580	0.2633	0.3637	0.092
H(37)	2*a*	0.2682	0.5817	0.3165	0.080
H(39A)	2*a*	0.2446	1.0637	0.2062	0.086
H(39B)	2*a*	0.2327	0.9462	0.2634	0.086
H(40A)	2*a*	0.1134	0.7840	0.1618	0.155
H(40B)	2*a*	0.0565	0.9253	0.2063	0.155
H(40C)	2*a*	0.1019	0.6652	0.2189	0.155

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*a*	0.8675(4)	1.334(1)	0.1635(2)	0.070(3)	0.072(3)	0.068(3)	0.002(3)	0.006(2)	0.017(3)
C(2)	2*a*	0.8210(4)	1.1426(9)	0.1372(2)	0.065(3)	0.071(3)	0.056(2)	0.009(2)	0.006(2)	0.004(2)
C(3)	2*a*	0.7773(3)	0.9651(7)	0.1766(1)	0.036(2)	0.031(2)	0.060(2)	0.001(1)	–0.009(1)	–0.007(1)
C(4)	2*a*	0.7982(4)	1.046(1)	0.2279(2)	0.061(2)	0.082(3)	0.058(2)	0.018(3)	0.011(2)	0.003(2)
C(5)	2*a*	0.7685(4)	0.900(1)	0.2736(2)	0.086(3)	0.086(4)	0.075(2)	0.021(3)	0.017(2)	0.011(2)
C(6)	2*a*	0.7912(4)	0.952(1)	0.3243(2)	0.079(3)	0.091(4)	0.075(3)	0.028(3)	0.018(2)	0.012(3)
C(7)	2*a*	0.7701(4)	0.804(1)	0.3722(2)	0.057(2)	0.083(3)	0.068(2)	0.020(2)	0.023(2)	0.009(2)
C(8)	2*a*	0.7002(4)	0.600(1)	0.3686(2)	0.060(2)	0.090(3)	0.050(2)	0.017(2)	0.005(2)	–0.008(2)
C(9)	2*a*	0.6857(3)	0.4581(9)	0.4146(2)	0.050(2)	0.069(3)	0.070(3)	0.001(2)	0.010(2)	–0.011(2)
C(10)	2*a*	0.7453(3)	0.5292(8)	0.4651(1)	0.046(2)	0.053(2)	0.050(2)	0.006(2)	0.012(2)	–0.000(2)
C(11)	2*a*	0.8145(3)	0.7348(8)	0.4694(2)	0.041(2)	0.048(2)	0.062(2)	0.007(2)	0.014(2)	0.003(2)
C(12)	2*a*	0.8267(3)	0.8707(9)	0.4230(2)	0.052(2)	0.065(3)	0.071(3)	0.007(2)	0.015(2)	0.013(2)
C(13)	2*a*	0.8629(3)	0.7568(7)	0.5264(2)	0.045(2)	0.044(2)	0.064(2)	0.002(2)	0.014(2)	0.002(2)
C(14)	2*a*	0.9367(3)	0.9160(9)	0.5563(2)	0.046(2)	0.057(3)	0.094(3)	–0.003(2)	0.014(2)	0.003(2)
C(15)	2*a*	0.9628(3)	0.887(1)	0.6130(2)	0.049(2)	0.085(4)	0.083(3)	–0.005(3)	–0.009(2)	–0.017(3)
C(16)	2*a*	0.9187(4)	0.695(1)	0.6392(2)	0.053(2)	0.096(4)	0.063(2)	–0.004(3)	0.004(2)	–0.006(3)
C(17)	2*a*	0.8492(3)	0.532(1)	0.6109(2)	0.056(2)	0.080(3)	0.061(2)	–0.001(3)	0.013(2)	0.004(2)
C(18)	2*a*	0.8204(3)	0.5609(8)	0.5539(2)	0.042(2)	0.058(3)	0.060(2)	0.000(2)	0.014(2)	–0.004(2)
C(19)	2*a*	0.6769(3)	0.2304(8)	0.5318(2)	0.057(2)	0.051(3)	0.074(3)	–0.007(2)	0.015(2)	0.000(2)
C(20)	2*a*	0.5668(4)	0.319(1)	0.5491(2)	0.068(3)	0.084(4)	0.097(3)	–0.011(3)	0.031(2)	–0.006(3)
C(21)	2*a*	0.9211(4)	0.611(1)	–0.0460(2)	0.068(3)	0.098(4)	0.090(3)	–0.004(3)	0.030(3)	–0.003(3)
C(22)	2*a*	0.8740(4)	0.802(1)	–0.0745(2)	0.080(3)	0.100(4)	0.068(3)	–0.026(3)	0.023(2)	0.007(3)
C(23)	2*a*	0.7755(4)	0.8907(9)	–0.0532(2)	0.072(3)	0.064(3)	0.058(2)	–0.010(2)	0.004(2)	0.011(2)
C(24)	2*a*	0.7481(3)	0.7618(8)	–0.0102(2)	0.056(2)	0.061(3)	0.049(2)	–0.008(2)	0.001(2)	–0.007(2)
C(25)	2*a*	0.6537(3)	0.7954(9)	0.0212(1)	0.058(2)	0.060(3)	0.052(2)	0.000(2)	0.003(2)	–0.007(2)
C(26)	2*a*	0.6259(3)	0.6496(8)	0.0601(1)	0.054(2)	0.065(3)	0.050(2)	0.003(2)	0.007(2)	0.006(2)
C(27)	2*a*	0.5393(3)	0.6815(8)	0.0976(2)	0.050(2)	0.056(3)	0.049(2)	0.003(2)	0.001(2)	0.001(2)
C(28)	2*a*	0.4613(3)	0.8705(8)	0.0923(2)	0.062(2)	0.061(3)	0.052(2)	0.001(2)	0.005(2)	0.003(2)
C(29)	2*a*	0.3850(3)	0.9080(8)	0.1292(2)	0.060(2)	0.057(3)	0.067(2)	0.013(2)	0.005(2)	0.000(2)
C(30)	2*a*	0.3877(3)	0.7504(8)	0.1734(2)	0.051(2)	0.050(2)	0.055(2)	0.001(2)	0.004(2)	–0.007(2)
C(31)	2*a*	0.4647(3)	0.5585(8)	0.1797(1)	0.043(2)	0.049(2)	0.049(2)	–0.002(2)	0.004(1)	–0.006(2)
C(32)	2*a*	0.5398(3)	0.5229(8)	0.1411(1)	0.046(2)	0.050(2)	0.056(2)	–0.001(2)	0.004(2)	–0.004(2)
C(33)	2*a*	0.4481(3)	0.4404(7)	0.2307(1)	0.044(2)	0.052(2)	0.049(2)	0.002(2)	0.005(2)	–0.002(2)
C(34)	2*a*	0.4996(3)	0.2434(9)	0.2594(2)	0.049(2)	0.075(3)	0.062(2)	0.002(2)	0.008(2)	0.003(2)
C(35)	2*a*	0.4662(4)	0.181(1)	0.3088(2)	0.068(3)	0.082(4)	0.063(2)	0.002(3)	0.007(2)	0.015(2)
C(36)	2*a*	0.3796(4)	0.309(1)	0.3300(2)	0.075(3)	0.096(4)	0.061(2)	–0.014(3)	0.017(2)	0.000(3)
C(37)	2*a*	0.3259(4)	0.4990(9)	0.3022(2)	0.067(2)	0.075(4)	0.061(2)	–0.002(3)	0.020(2)	–0.013(2)
C(38)	2*a*	0.3604(3)	0.5645(8)	0.2522(2)	0.055(2)	0.055(3)	0.053(2)	–0.005(2)	0.007(2)	–0.012(2)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(39)	2*a*	0.2323(4)	0.9137(9)	0.2244(2)	0.067(3)	0.066(3)	0.083(3)	0.017(2)	0.020(2)	–0.014(2)
C(40)	2*a*	0.1150(4)	0.813(1)	0.2006(3)	0.063(3)	0.115(5)	0.133(4)	0.008(4)	0.010(3)	–0.016(4)
N(1)	2*a*	0.7490(3)	0.4252(7)	0.5163(1)	0.055(2)	0.056(2)	0.060(2)	–0.010(2)	0.013(2)	–0.003(2)
N(2)	2*a*	0.3242(3)	0.7528(6)	0.2175(1)	0.055(2)	0.052(2)	0.060(2)	0.005(2)	0.015(2)	–0.010(2)
S(1)	2*a*	0.8629(1)	1.3138(3)	0.23193(5)	0.107(1)	0.0751(9)	0.0745(7)	–0.0025(8)	0.0020(7)	–0.0034(7)
S(2)	2*a*	0.8453(1)	0.5321(3)	0.00521(5)	0.0755(7)	0.087(1)	0.0858(8)	0.0160(7)	0.0285(6)	0.0211(8)

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