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Structure of a 1:2 Electron Donor-Acceptor Complex of 9,9′-Diethyl-3,3′-di-9*H*-carbazolyl and Tetracyanoethylene

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In the title electron donor-acceptor complex, $C_{28}H_{24}N_2 \cdot 2C_6N_4$, the 9,9′-diethyl-3,3′-di-9*H*-carbazolyl molecule lies on a crystallographic inversion center, which is located at the mid-point of the C3-C3′ bond. In the crystal structure, two TCNE molecules are located above and below the central rings of the two neighboring donor molecules. The donor molecule is planar with a dihedral angle between the planes of each carbazolyl groups of 0.08(8)°. The molecular packing is stabilized mainly by donor-acceptor π-π interactions.

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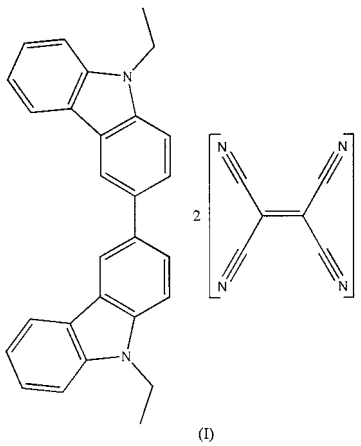
Electron donor-acceptor (EDA) complexes of carbazoles have drawn much interest due to their application in the industry as photoconductors. Studies on the EDA complexes of some low-molecular-weight models of polyvinylcarbazole (PVK) have been conducted to understand the nature of the complexation, both in solution and in the solid state.[1,2] We report the results of a single-crystal X-ray diffraction analysis of an EDA complex of 9,9′-diethyl-3,3′-di-9*H*-carbazolyl with TCNE, which was carried out to determine the intermolecular relations, molecular geometry, and stoichiometry of the complexation.

9,9′-Diethyl-3,3′-di-9*H*-carbazolyl was prepared according to a literature procedure *via* the oxidation of 9-ethylcarbazole (Aldrich) by ferric chloride.[3] TCNE (Aldrich) was purified by successive sublimations. Dark-blue crystals of the EDA complex of 9,9′-diethyl-3,3′-di-9*H*-carbazolyl with TCNE were grown from a concentrated solution (1:1 donor:acceptor molar ratio) in dichloromethane by slow evaporation at room temperature. Crystals of the title complex were separated manually from colorless crystals of uncomplexed TCNE.



(I)

Fig. 1 Chemical structure of I.

The title complex (I) (Fig. 1) crystallizes in a 1:2 9,9′-diethyl-3,3′-di-9*H*-carbazolyl/TCNE ratio (1:1 donor group:acceptor molecule ratio). The crystal and experimental data are given in Table 1. The rather high values of *R* and *wR*2 are ascribed to the poor quality of the crystal due to the decomposition of TCNE at

Table 1 Crystal and experimental data

Empirical formula: $C_{28}H_{24}N_2 \cdot 2(C_6N_4)$	
Formula weight: 644.68	
Wavelength: 0.71073 Å	
Temperature: 295(2)K	
Space group: $P2_1/n$	$Z = 4$
$a = 7.1150(9)$Å	
$b = 23.4740(8)$Å	
$c = 9.615(2)$Å	$\beta = 98.1780(10)^\circ$
$V = 1589.5(4)$Å^3	
$D_x = 1.347$ g/cm^3	
No. of reflections used = 2806	
$2\theta_{max} = 50.2^\circ$ with Mo K_α	
$R[F^2 > 2\sigma(F^2)] = 0.095$	
$wR(F^2) = 0.274$	
$S = 1.04$	
$(\Delta/\sigma)_{max} < 0.001$	
$(\Delta\rho)_{max} = 0.32$ e Å^{-3}	
$(\Delta\rho)_{min} = -0.43$ e Å^{-3}	
Measurement: Enraf-Nonius CAD4	
Data collection and cell refinement: CAD-4-PC Software	
Structure determination: direct method (SIR92)	
Structure refinement: full matrix least squares on F^2 (SHELXL97)	
Molecular graphics: ORTEP-3 for Windows and PLUTON	
Publication material: WinGX	

CCDC 672058 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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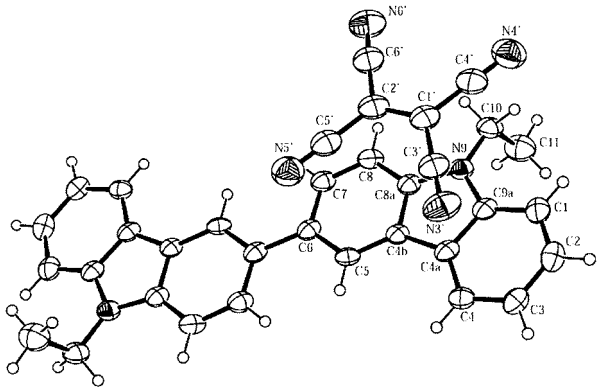

Fig. 2 Structure of (I) along with the atom numbering scheme (displacement ellipsoids drawn at the 40% probability level; arbitrary spheres for the H atoms; unlabeled atoms are related to labeled atoms by (–*x*+1, –*y*, –*z*)).

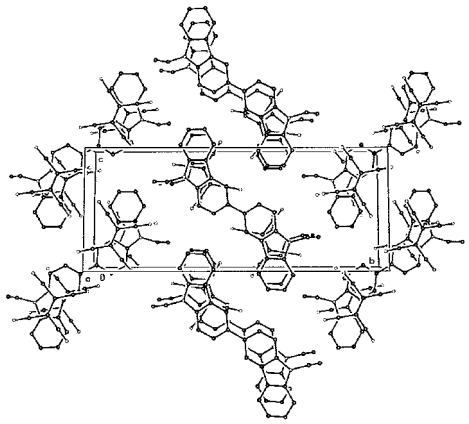

Fig. 3 Molecular packing of I. H atoms excluded for clarity.

room temperature. All non-hydrogen atoms were refined anisotropically. All H atoms were fixed geometrically and allowed to ride on their corresponding parent atoms with C–H distances in the range of 0.93 – 0.97 Å with U_{iso}(H) = 1.5U_{eq}(C) of the parent atom for the methyl groups and 1.2U_{eq}(C) for the remainder. The asymmetric unit contains one TCNE and one-half 9,9′-diethyl-3,3′-di-9*H*-carbazolyl molecules. The other half of 9,9′-diethyl-3,3′-di-9*H*-carbazolyl is generated by a center of inversion. The bond lengths and angles of the carbazole groups and the TCNE molecule in the complex are comparable to those of a related complex reported in the literature.[4] Each of the carbazole skeletons and the TCNE molecule (Fig. 2) are essentially planar, with r.m.s deviations of 0.035 (labeled ring), 0.036 (unlabeled ring) and 0.016 Å (TCNE). The dihedral angle of 0.08(8)° between the planes of the carbazole groups in 9,9′-diethyl-3,3′-di-9*H*-carbazolyl indicates how the bichromophoric molecule arranged itself to a more favorable geometry for complex formation. The interplanar dihedral angle between the carbazole groups of the uncomplexed 9,9′-diethyl-3,3′-di-9*H*-carbazolyl was 40.38(4)°.[5] The molecular packing of (I) (Fig. 3) is mainly determined by π-π interactions between the central ring of the carbazole groups and the TCNE molecules. One carbazole group associates with two TCNE molecules on each side with angles of 5.01(7)° (mean interplanar distance, 3.24 Å; centroid separation; 3.470 Å; vertical displacement between the centroids; 1.23 Å) and 5.09(7)° (mean interplanar distance, 3.41 Å; centroid separation, 3.683 Å; vertical displacement between the centroids, 1.40 Å), respecitvely. A similar π-π overlap was found in the complex between 9-ethylcarbazole and TCNE having dihedral angles of 4.5° and 2.7° and distances of 3.24 Å between the mean planes of the carbazole moiety and TCNE molecules on each side.

Table 2 Selected bond lengths (Å), angles (°) and torsion angles (°)

N9—C9A	1.389(4)	C7—C8	1.359(5)
N9—C10	1.445(4)	C8—C8A	1.403(5)
C1—C2	1.374(5)	C10—C11	1.495(6)
C1—C9A	1.388(5)	C1'—C2'	1.365(6)
C2—C3	1.386(6)	C1'—C4'	1.421(7)
C3—C4	1.379(5)	C1'—C3'	1.428(6)
C4—C4A	1.402(5)	C2'—C5'	1.440(6)
C4A—C9A	1.401(5)	C2'—C6'	1.442(6)
C4A—C4B	1.450(5)	C3'—N3'	1.141(5)
C4B—C5	1.390(5)	C4'—N4'	1.119(6)
C4B—C8A	1.407(5)	C5'—N5'	1.128(5)
C5—C6	1.408(5)	C6'—N6'	1.127(5)
C6—C7	1.409(5)		
C1—C2—C3	121.9(3)	C1—C9A—C4A	121.3(3)
C3—C4—C4A	117.8(3)	N9—C9A—C4A	109.6(3)
C9A—C4A—C4	120.2(3)	N9—C10—C11	113.0(3)
C9A—C4A—C4B	106.5(3)	C2'—C1'—C4'	120.1(4)
C4—C4A—C4B	133.3(3)	C2'—C1'—C3'	122.1(4)
C5—C4B—C8A	120.2(3)	C4'—C1'—C3'	117.8(4)
C5—C4B—C4A	133.5(3)	C1'—C2'—C5'	122.8(4)
C8A—C4B—C4A	106.3(3)	C1'—C2'—C6'	119.3(4)
C4B—C5—C6	120.6(3)	C5'—C2'—C6'	118.3(4)
C7—C6—C5	116.9(3)	N3'—C3'—C1'	179.1(5)
C7—C6—C6'	121.9(4)	N4'—C4'—C1'	179.2(5)
C5—C6—C6'	121.1(4)	N5'—C5'—C2'	179.5(5)
C8—C7—C6	123.8(3)	N6'—C6'—C2'	176.5(5)
C7—C8—C8A	118.6(3)		
C8A—N9—C10—C11	–92.7(4)	C3'—C1'—C2'—C6'	–179.4(3)
C9A—N9—C10—C11	72.1(5)	C4'—C1'—C2'—C5'	177.7(3)

Symmetry codes: (i) –*x*+1, –*y*, –*z*.

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