Charge-transfer complexes of N-methyl-and N-ethylcarbazole with 3,5-dinitrobenzonitrile

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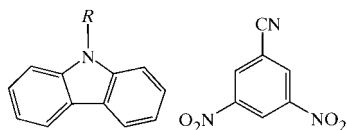Correspondence e-mail: ohba@chem.keio.ac.jp

In the two title compounds, N-methylcarbazole–3,5-dinitro-benzonitrile (1/1), $C_{13}H_{11}N \cdot C_7H_3N_3O_4$, (I), and N-ethylcarba-zole–3,5-dinitrobenzonitrile (1/1), $C_{14}H_{13}N \cdot C_7H_3N_3O_4$, (II), the donor and acceptor molecules are stacked alternately to form one-dimensional columns. In (I), the N-methyl group of the donor is nearly eclipsed with respect to one of the nitro groups of the neighboring acceptor in a column, whereas the N-ethyl group is *anti* with respect to the cyano group of the neighboring acceptor in (II).

Comment

Crystals of (I) underwent photoredox reactions initiated by the excited nitro group, leading to α-oxidation of the N-alkyl groups. However, no photoreaction was observed for (II) (Ito *et al.*, 1998).

(I) R = methyl
(II) R = ethyl

In (I), the N-methyl group of the donor is nearly eclipsed with respect to one of the nitro groups of the neighboring acceptor in a column, whereas the N-ethyl group is *anti* with respect to the cyano group of the neighboring acceptor in (II).

Experimental

Equimolecular mixtures of N-alkylcarbazoles and 3,5-dinitrobenzo-nitrile were recrystallized from methylene chloride [for (I)] and ethyl acetate [for (II)].

Compound (I)

Crystal data

$C_{13}H_{11}N \cdot C_7H_3N_3O_4$	$D_x = 1.382$ Mg m^{-3}
$M_r = 374.35$	Mo $K\alpha$ radiation
Orthorhombic, $P2_12_12_1$	Cell parameters: 25 reflns
$a = 8.339$ (2) Å	$\theta = 10–15°$
$b = 27.604$ (4) Å	$\mu = 0.099$ mm^{-1}
$c = 7.817$ (2) Å	$T = 293$ (1) K
$V = 1799.4$ (7) Å^3	Prism, red
$Z = 4$	$0.55 \times 0.30 \times 0.20$ mm

Data collection

Rigaku AFC-5 diffractometer	$h = 0 \rightarrow 10$
ω scans	$k = 0 \rightarrow 35$
2384 measured reflections	$l = 0 \rightarrow 10$
2384 independent reflections	3 standard reflections
1034 reflections with $I > 2\sigma(I)$	every 100 reflections
$\theta_{max} = 27.5°$	intensity decay: 1.1%

Refinement

Refinement on F^2	H-atom parameters not refined
$R(F) = 0.063$	$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2]$
$wR(F^2) = 0.162$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.001$
2384 reflections	$\Delta\rho_{max} = 0.21$ e Å^{-3}
253 parameters	$\Delta\rho_{min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

O1—N5	1.218 (9)	N7—C9	1.099 (9)
O2—N5	1.209 (9)	N8—C28	1.475 (7)
O3—N6	1.204 (7)	C9—C10	1.462 (9)
O4—N6	1.212 (7)		
O1—N5—O2	124.5 (7)	N7—C9—C10	177.3 (7)
O3—N6—O4	123.5 (6)		

Compound (II)

Crystal data

$C_{14}H_{13}N \cdot C_7H_3N_3O_4$	$D_x = 1.368$ Mg m^{-3}
$M_r = 388.38$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters: 25 reflections
$a = 16.227$ (2) Å	$\theta = 10.0–15.0°$
$b = 6.982$ (2) Å	$\mu = 0.097$ mm^{-1}
$c = 17.435$ (2) Å	$T = 293$ (1) K
$\beta = 107.30$ (1)°	Prism, orange
$V = 1886.0$ (6) Å^3	$0.50 \times 0.35 \times 0.30$ mm
$Z = 4$	

Data collection

Rigaku AFC-5 diffractometer	$h = 0 \rightarrow 21$
$\theta–2\theta$ scans	$k = 0 \rightarrow 9$
4482 measured reflections	$l = -22 \rightarrow 22$
4322 independent reflections	3 standard reflections
1585 reflections with $I > 2\sigma(I)$	every 100 reflections
$R_{int} = 0.020$	intensity decay: 2.8%
$\theta_{max} = 27.5°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2]$
$R(F) = 0.064$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.160$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.97$	$\Delta\rho_{max} = 0.13$ e Å^{-3}
4322 reflections	$\Delta\rho_{min} = -0.13$ e Å^{-3}
263 parameters	Extinction correction: *SHELXL*97
H-atom parameters not refined	Extinction coefficient: 0.0071 (10)

Table 2
Selected geometric parameters (Å, °) for (II).

O1—N5	1.219 (4)	N8—C28	1.463 (5)
O2—N5	1.225 (5)	C9—C10	1.447 (6)
O3—N6	1.222 (5)	C28—C29	1.506 (6)
O4—N6	1.216 (5)		
N7—C9	1.123 (6)		
O1—N5—O2	123.9 (3)	N7—C9—C10	179.0 (4)
O3—N6—O4	124.5 (3)	N8—C28—C29	111.5 (3)

All H-atom positional parameters were calculated geometrically and fixed with $U_{iso}(H) = 1.2U_{eq}$(parent atom).

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *TEXSAN*.

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