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Charge-transfer complexes of *N*-methyl-, *N*-isopropyl-, *N*-butyl- and *N*-isobutylcarbazole with 3,5-dinitrobenzoic acid

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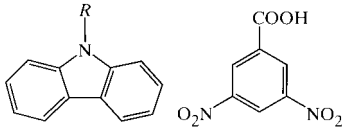
In the title four compounds, $C_{13}H_{11}N{\cdot}C_7H_4N_2O_6$, (I), $C_{15}H_{15}N{\cdot}C_7H_4N_2O_6$, (II), $C_{16}H_{17}N{\cdot}C_7H_4N_2O_6$, (III), and $C_{16}H_{17}N{\cdot}C_7H_4N_2O_6$, (IV), the donor and acceptor molecules are stacked alternately to form one-dimensional columns. In (I), the *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*-isopropyl, *N*-butyl and *N*-isobutyl groups are in *anti* positions with respect to one of the nitro groups of the neighboring acceptor in compounds (II)–(IV).

Comment

Crystals of (I) underwent photoredox reactions initiated by the excited nitro group, leading to α-oxidation of the *N*-alkyl groups. Complexes (III) and (IV) were less photoreactive than (I), and no reaction was observed for (II) (Ito *et al.*, 1998).



(I) R = methyl
(II) R = isopropyl
(III) R = *n*-butyl
(IV) R = isobutyl

In (I), the *N*-methyl group of the donor is nearly eclipsed to one of the nitro groups of the neighboring acceptor in a column, whereas the *N*-isopropyl, *N*-butyl and *N*-isobutyl groups are in *anti* positions with respect to one of the nitro groups of the neighboring acceptor in (II)–(IV).

Experimental

Equimolar mixtures of *N*-alkylcarbazoles and 3,5-dinitrobenzoic acid were recrystallized from ethylacetate [for (I)], acetonitrile [for (II)–(III)] and acetone [for (IV)].

Compound (I)

Crystal data

$C_{13}H_{11}N{\cdot}C_7H_4N_2O_6$
M_r = 393.36
Triclinic, $P\overline{1}$
a = 8.414 (1) Å
b = 15.763 (2) Å
c = 6.991 (1) Å
α = 91.82 (1)°
β = 99.91 (1)°
γ = 81.59 (1)°
V = 903.6 (2) Å^3
Z = 2
D_x = 1.446 Mg m^{-3}
Cell parameters from 25 reflections
θ = 14.8–15.0°
μ = 0.109 mm^{-1}
T = 298 (1) K
Plate, orange
0.6 × 0.4 × 0.1 mm

Data collection

Rigaku AFC-7*R* diffractometer
θ–2θ scans
5045 measured reflections
4128 independent reflections
2977 reflections with $I > 2\sigma(I)$
R_{int} = 0.005
θ_{max} = 27.5°
$h = -6 \rightarrow 11$
$k = -20 \rightarrow 20$
$l = -9 \rightarrow 9$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.044
$wR(F^2)$ = 0.147
S = 1.08
4128 reflections
270 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0715P)^2 + 0.1508P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

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

O1—C10	1.260 (2)	O5—N8	1.214 (2)
O2—C10	1.265 (2)	O6—N8	1.222 (2)
O3—N7	1.213 (2)	N9—C29	1.449 (2)
O4—N7	1.220 (2)		
O3—N7—O4	124.5 (2)	O1—C10—C11	117.8 (1)
O5—N8—O6	123.8 (2)	O2—C10—C11	117.7 (2)
O1—C10—O2	124.4 (1)		

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	0.73 (5)	1.92 (5)	2.648 (2)	172 (5)
O2—H2···O1^{i}	0.88 (5)	1.77 (5)	2.648 (2)	179 (5)

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

Compound (II)

Crystal data

$C_{15}H_{15}N{\cdot}C_7H_4N_2O_6$
M_r = 421.41
Monoclinic, $P2_1/a$
a = 8.504 (2) Å
b = 29.533 (4) Å
c = 8.568 (2) Å
β = 108.05 (2)°
V = 2045.8 (7) Å^3
Z = 4
D_x = 1.368 Mg m^{-3}
Cell parameters from 25 reflections
θ = 12.9–14.9°
μ = 0.101 mm^{-1}
T = 298 (1) K
Prism, orange
0.5 × 0.5 × 0.5 mm

Data collection

Rigaku AFC-7R diffractometer
ω scans
4990 measured reflections
4685 independent reflections
3283 reflections with $I > 2\sigma(I)$
R_{int} = 0.011
θ_{max} = 27.5°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 38$
$l = -11 \rightarrow 11$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.041
$wR(F^2)$ = 0.122
S = 1.05
4685 reflections
288 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 0.4038P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

O1—C10	1.251 (2)	O6—N8	1.215 (2)
O2—C10	1.266 (2)	N9—C29	1.474 (2)
O3—N7	1.216 (3)	C29—C30	1.518 (3)
O4—N7	1.214 (2)	C29—C31	1.521 (3)
O5—N8	1.215 (2)		
O3—N7—O4	124.1 (2)	O1—C10—C11	118.1 (1)
O5—N8—O6	124.8 (2)	O2—C10—C11	117.1 (1)
O1—C10—O2	124.8 (1)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	0.78 (4)	1.86 (4)	2.629 (2)	174 (5)
O2—H2···O1^{i}	0.82 (4)	1.81 (4)	2.629 (2)	178 (4)

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

Compound (III)

Crystal data

$C_{16}H_{17}N{\cdot}C_7H_4N_2O_6$
M_r = 435.44
Triclinic, $P\overline{1}$
a = 16.723 (2) Å
b = 16.784 (3) Å
c = 8.4129 (9) Å
α = 102.36 (1)°
β = 92.34 (1)°
γ = 109.91 (1)°
V = 2152.0 (6) Å^3
Z = 4
D_x = 1.344 Mg m^{-3}
Cell parameters from 25 reflections
θ = 11.8–14.7°
μ = 0.099 mm^{-1}
T = 298 (1) K
Prism, orange
0.6 × 0.5 × 0.2 mm

Data collection

Rigaku AFC-7R diffractometer
θ–2θ scans
10 208 measured reflections
9870 independent reflections
4817 reflections with $I > 2\sigma(I)$
R_{int} = 0.010
θ_{max} = 27.5°
$h = 0 \rightarrow 22$
$k = -22 \rightarrow 22$
$l = -11 \rightarrow 11$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.061
$wR(F^2)$ = 0.192
S = 1.74
9870 reflections
593 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0500P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for (III).

O1—C10	1.272 (4)	O6—N8	1.215 (4)
O1*—C10*	1.281 (4)	O6*—N8*	1.211 (4)
O2—C10	1.249 (3)	N9—C29	1.465 (4)
O2*—C10*	1.247 (3)	N9*—C29*	1.448 (3)
O3—N7	1.199 (4)	C29—C30	1.495 (4)
O3*—N7*	1.221 (3)	C29*—C30*	1.504 (4)
O4—N7	1.211 (5)	C30—C31	1.529 (4)
O4*—N7*	1.214 (4)	C30*—C31*	1.512 (4)
O5—N8	1.211 (4)	C31—C32	1.471 (4)
O5*—N8*	1.207 (4)	C31*—C32*	1.472 (5)
O3—N7—O4	123.9 (3)	O1—C10—C11	116.3 (2)
O3*—N7*—O4*	124.3 (3)	O2—C10—C11	118.5 (3)
O5—N8—O6	124.0 (2)	O1*—C10*—O2*	125.5 (3)
O5*—N8*—O6*	124.1 (2)	O1*—C10*—C11*	115.7 (2)
O1—C10—O2	125.2 (3)	O2*—C10*—C11*	118.8 (3)

Table 6
Hydrogen-bonding geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2*	0.64 (7)	2.02 (7)	2.651 (4)	171 (6)
O1*—H1*···O2	0.86 (6)	1.82 (6)	2.637 (4)	158 (5)
O2—H2···O1*	0.74 (8)	1.90 (8)	2.637 (4)	169 (8)
O2*—H2*···O1	1.01 (8)	1.65 (8)	2.651 (4)	170 (6)

Compound (IV)

Crystal data

$C_{16}H_{17}N{\cdot}C_7H_4N_2O_6$
M_r = 435.44
Monoclinic, $P2_1/c$
a = 8.212 (2) Å
b = 31.924 (2) Å
c = 8.438 (1) Å
β = 106.54 (1)°
V = 2120.5 (6) Å^3
Z = 4
D_x = 1.364 Mg m^{-3}
Cell parameters from 25 reflections
θ = 12.3–14.7°
μ = 0.100 mm^{-1}
T = 298 (1) K
Prism, orange
0.5 × 0.4 × 0.3 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω scans
5184 measured reflections
4864 independent reflections
2811 reflections with $I > 2\sigma(I)$
R_{int} = 0.006
θ_{max} = 27.5°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 41$
$l = -11 \rightarrow 0$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.049
$wR(F^2)$ = 0.165
S = 1.03
4864 reflections
298 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 1.8479P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0044 (7)

Table 7
Selected geometric parameters (Å, °) for (IV).

O1—C10	1.269 (3)	O6—N8	1.220 (4)
O2—C10	1.253 (4)	N9—C29	1.464 (4)
O3—N7	1.212 (4)	C29—C30	1.519 (3)
O4—N7	1.212 (4)	C30—C31	1.516 (4)
O5—N8	1.215 (3)	C30—C32	1.509 (4)
O3—N7—O4	124.0 (3)	O1—C10—C11	117.0 (2)
O5—N8—O6	124.7 (3)	O2—C10—C11	118.3 (2)
O1—C10—O2	124.7 (2)		

Table 8
Hydrogen-bonding geometry (Å, °) for (IV).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	0.80 (6)	1.87 (7)	2.650 (3)	165 (8)
O2—H2···O1^{i}	0.90 (8)	1.76 (8)	2.650 (3)	171 (9)

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

In compounds (I)–(IV), the 3,5-dinitrobenzoic acid molecules form a dimeric structure with cyclic hydrogen bonds. The acid proton has two possible positions with site-occupation factors of 50%. They were located from difference syntheses and refined isotropically. The O—H bond lengths are 0.73 (5)–0.88 (5) Å for (I), 0.78 (4)–0.82 (4) Å for (II), 0.64 (7)–1.01 (8) Å for (III) and 0.80 (6)–0.90 (8) Å for (IV). The other H-atom positional parameters were calculated geometrically and fixed with U_{iso}(H) = 1.2U_{eq}(parent atom).

For all 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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *TEXSAN*.

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