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The Potassium Salt of 9-(2,4,6-Trinitroanilino)carbazole

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Abstract

The picryl ring in the potassium salt of 9-(2,4,6-trinitroanilino)carbazole [potassium N-(9-carbazolyl)-2,4,6-trinitroanlidide, $K^+.C_{18}H_{10}N_5O_6^-$] is in a boat conformation. The C—N bond between C1 of the picryl ring and the adjacent N atom of the hydrazine moiety is shortened, indicating delocalization of the -1 charge into the picryl ring system. The K^+ ion, which has replaced the proton on the N atom bonded to C1, is ionically bonded to this N atom and to an O atom in an *ortho* nitro group of the parent molecule. K^+ also coordinates with four O atoms from three other molecules and with the π cloud of a phenyl ring of the carbazole group of a fourth molecule.

Comment

It has long been known that addition of bases to solutions of 2,2-diphenyl-1-picrylhydrazine (DH) and 9-(2,4,6-trinitroanilino)carbazole (AH) results in the removal of the hydrazinic protons. The pK_a's of DH and AH in methanol/thf are 8.94 (6) and 7.96 (5), respectively (Nelson, 1994). Whereas X-ray crystallographic analyses show that the picryl rings in both hydrazines

are essentially planar (Wang, Barton, Robertson & Weil, 1991; Wang, Barton, Robertson, Weil & Brown, 1987), X-ray analysis of the potassium salt of DH, K^+D^-, shows that the picryl ring is severely distorted (into a twist-boat conformation) due to the presence of ionic bonding between K^+ and N4 and O1 of the anion (Gopal, Robertson & Weil, 1983). The present structural study was undertaken to determine if similar ionic bonding and distortion of the picryl ring is observed in the potassium salt of AH. The important resonance structures of the A^- anion contributing to the electronic structure of this species in its ground state are similar to the resonance structures of the D^- anion (Gopal, Robertson & Weil, 1983) and are illustrated in Fig. 1.
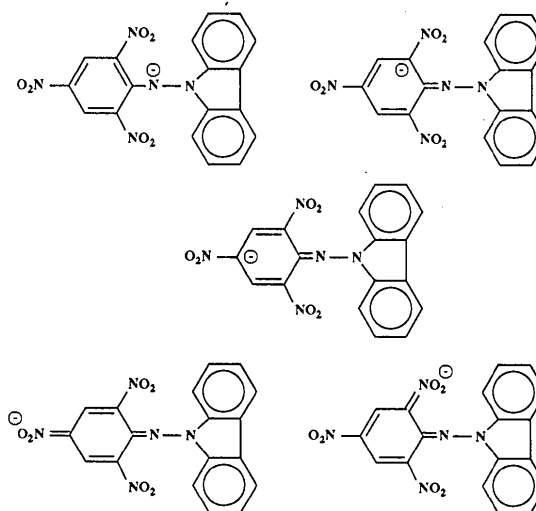

Fig. 1. Resonance structures for the A^- ion.

The X-ray structure determination of the title compound (Fig. 2) shows that the picryl ring has the boat form; the least-squares planes through C1, C2 and C6 and through C3, C4 and C5 are inclined at 18.8 (2) and 9.3 (2)°, respectively, to the least-squares plane through C2, C3, C5 and C6. The hydrazine linkage to the picryl ring is nearly coplanar with the plane through C1, C2 and C6, and the carbazole moiety is rotated by 49.0 (1)° with respect to the plane through C2, C3, C5 and C6 to minimize steric interaction between it and the nitro group at C6.

The plane of the nitro group at C2 is rotated by 17.5 (1)° with respect to the least-squares plane through C2, C3, C5 and C6, while the nitro group at C6 is rotated by 34.4 (1)° with respect to the same plane. The nitro group at C4 is rotated by 9.7 (2)° with respect to the plane through C3, C4 and C5. The different rotation angles for the nitro groups probably occur in order to optimize the geometry of coordination to K^+ in the crystal structure. This ionic bonding constrains the C2 nitro group to be almost coplanar with C1,
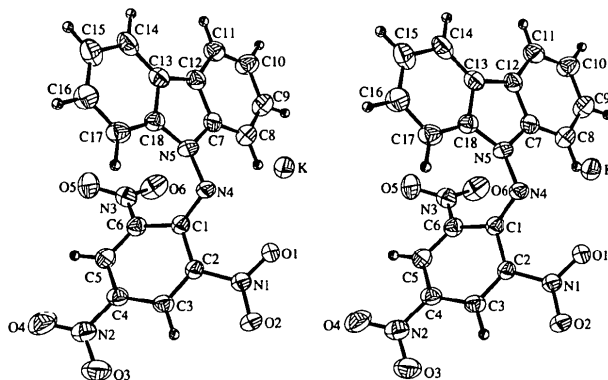
Fig. 2. Stereoscopic view of the title compound with displacement ellipsoids drawn at the 50% probability level for the non-H atoms. H atoms are drawn as small spheres of arbitrary size.

C2 and C6. The out-of-plane rotation angle of the nitro group at C6 is much the same as that in K^+D^- despite the different phenyl ring configurations in the two molecules. In addition to coordinating with N4 and O1 through ionic bonding, the K^+ ion also coordinates with four O atoms (O1^i, O2^i, O3^{ii} and O5^{iii}) from three other molecules in the crystal lattice and with the π cloud of a phenyl ring (C7^{iv}, C8^{iv}, C9^{iv}, C10^{iv}, C11^{iv} and C12^{iv}) of the carbazole group in a fourth molecule [symmetry codes: (i) $-x$, $-y$, $-z$; (ii) $x-\frac{1}{2}$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (iii) $\frac{1}{2}-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$; (iv) $x-\frac{1}{2}$, $\frac{1}{2}-y$, $z-\frac{1}{2}$]. The K^+ ion is positioned over a face of the phenyl ring, but is closest to C11^{iv} [3.290(3) Å] and furthest from C8^{iv} [4.086(3) Å]. The distances from K^+ to C10^{iv}, C11^{iv} and C12^{iv} are comparable [3.577(3), 3.290(3) and 3.403(3) Å, respectively].

The molecules are arranged in the crystal lattice with the electron-withdrawing picryl rings lying close to electron-donating phenyl rings of the carbazole moieties of adjacent molecules (Fig. 3). The shortest intermolecular C—C distances between the picryl ring C atoms and the C atoms of the nearest carbazole moiety, where the rings are approximately parallel, are C3—C10^v 3.53, C4—C10^v 3.55, C4—C11^v 3.54 and C5—C10^v 3.64 Å [symmetry code: (v) $x+\frac{1}{2}$, $\frac{1}{2}-y$, $z-\frac{1}{2}$]. These distances and the intense colour of $\bar{K}^+\bar{H}^-$ suggest
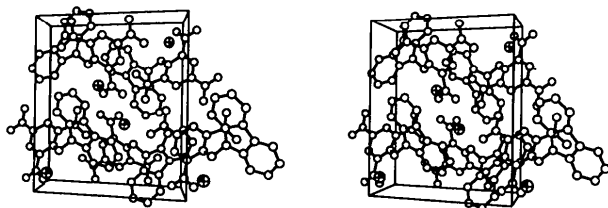
the presence of a moderately strong π-molecular donor–acceptor interaction between molecules.

The C1—N4 bond length in the anion, 1.303(3) Å, is 0.091 Å shorter than the average for a C_{Ar}—N single bond (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987) and is close to the C=N double-bond length of 1.287(4) Å in N-(diphenylmethylene)aniline at 113 K (Tucker, Hoekstra, ten Cate & Vos, 1975). This suggests that the negative charge on N4 is delocalized over the picryl ring system. The N4—N5 bond length of 1.413(2) Å compared with the N—N single-bond length of 1.390(8) Å at room temperature and 1.406(4) Å at 113 K in the structure of tetraphenylhydrazine (Hoekstra, Vos, Braun & Hornstra, 1975) suggests that N4—N5 is a single bond and that very little, if any, of the negative charge on N4 is delocalized over the carbazole moiety.

Experimental

The title compound was prepared by the addition of methanolic potassium ethanoate to a benzene solution of AH (Nelson, 1994). Crystals were grown from a solution of K^+A^- in acetone/diethyl ether.

Crystal data

$K^+.C_{18}H_{10}N_5O_6^-$	Mo $K\alpha$ radiation
$M_r = 431.40$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
$a = 10.8670$ (11) Å	$\theta = 8.50–18.00°$
$b = 13.7970$ (14) Å	$\mu = 0.35$ mm^{-1}
$c = 12.7190$ (13) Å	$T = 289$ K
$\beta = 113.320$ (11)°	Prism
$V = 1751.2$ (3) Å^3	$0.38 \times 0.25 \times 0.10$ mm
$Z = 4$	Black
$D_x = 1.636$ Mg m^{-3}	
$D_m = 1.633$ Mg m^{-3}	
D_m measured by flotation	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.010$
diffractometer	$\theta_{max} = 24.93°$
$\omega/2\theta$ scans	$h = -12 \rightarrow 11$
Absorption correction:	$k = 0 \rightarrow 16$
none	$l = 0 \rightarrow 15$
3513 measured reflections	3 standard reflections
3077 independent reflections	frequency: 120 min
3077 observed reflections	intensity variation: none

Refinement

|	
Refinement on F	$(\Delta/\sigma)_{max} < 0.001$
$R = 0.063$	$\Delta\rho_{max} = 0.30$ e Å^{-3}
$wR = 0.047$	$\Delta\rho_{min} = -0.31$ e Å^{-3}
$S = 1.00$	Extinction correction: none
3077 reflections	Atomic scattering factors
271 parameters	from International Tables
H-atom coordinates and U_{iso}	for X-ray Crystallography
not refined	(1974, Vol. IV, Table
$w = 1/[\sigma^2(F) + 0.0008F^2]$	2.2B)

Fig. 3. Stereoscopic drawing of the crystal packing with H atoms omitted for clarity. The origin is at the lower left-hand front corner; the a axis runs at an angle into the plane of the paper, the b axis is vertical and the c axis is horizontal.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
K	−0.0726 (1)	0.1125 (1)	0.0969 (1)	0.044 (1)
O1	0.1464 (2)	0.0637 (1)	0.0494 (1)	0.044 (1)
O2	0.2185 (2)	0.0604 (1)	−0.0848 (1)	0.057 (1)
O3	0.3491 (2)	0.3376 (1)	−0.2234 (1)	0.060 (1)
O4	0.3937 (2)	0.4708 (1)	−0.1266 (2)	0.063 (1)
O5	0.4105 (2)	0.4660 (1)	0.2635 (2)	0.058 (1)
O6	0.4205 (2)	0.3206 (1)	0.3290 (2)	0.061 (1)
N1	0.1977 (2)	0.1045 (1)	−0.0088 (2)	0.037 (1)
N2	0.3592 (2)	0.3850 (1)	−0.1384 (2)	0.044 (1)
N3	0.3877 (2)	0.3787 (1)	0.2504 (2)	0.042 (1)
N4	0.1543 (2)	0.2335 (1)	0.1576 (2)	0.037 (1)
N5	0.1515 (2)	0.2949 (1)	0.2455 (1)	0.038 (1)
C1	0.2354 (2)	0.2581 (1)	0.1093 (2)	0.033 (1)
C2	0.2377 (2)	0.2044 (1)	0.0112 (2)	0.033 (1)
C3	0.2774 (2)	0.2461 (2)	−0.0679 (2)	0.035 (1)
C4	0.3268 (2)	0.3401 (2)	−0.0515 (2)	0.036 (1)
C5	0.3592 (2)	0.3856 (2)	0.0540 (2)	0.037 (1)
C6	0.3237 (2)	0.3426 (2)	0.1338 (2)	0.035 (1)
C7	0.1627 (2)	0.2547 (1)	0.3490 (2)	0.037 (1)
C8	0.2146 (3)	0.1652 (2)	0.3939 (2)	0.047 (2)
C9	0.2209 (3)	0.1430 (2)	0.5025 (2)	0.053 (2)
C10	0.1761 (3)	0.2087 (2)	0.5628 (2)	0.052 (2)
C11	0.1236 (3)	0.2974 (2)	0.5168 (2)	0.047 (2)
C12	0.1168 (2)	0.3218 (2)	0.4075 (2)	0.038 (1)
C13	0.0725 (2)	0.4056 (2)	0.3353 (2)	0.038 (1)
C14	0.0178 (3)	0.4949 (2)	0.3455 (2)	0.050 (2)
C15	−0.0105 (3)	0.5623 (2)	0.2608 (2)	0.055 (2)
C16	0.0133 (3)	0.5432 (2)	0.1636 (2)	0.050 (1)
C17	0.0646 (2)	0.4550 (2)	0.1482 (2)	0.044 (1)
C18	0.0943 (2)	0.3866 (2)	0.2344 (2)	0.035 (1)

Table 2. *Selected geometric parameters* $(\text{Å}, °)$

K—O1	2.761 (2)	N5—N4	1.413 (2)
K—N4	2.820 (2)	N5—C18	1.392 (3)
K—O1^i	2.973 (2)	C2—C1	1.460 (3)
K—O2^i	2.835 (2)	C2—C3	1.368 (3)
K—O3^{ii}	2.822 (2)	C3—C4	1.388 (3)
K—O5^{iii}	2.804 (2)	C5—C4	1.396 (3)
K—C7^{iv}	3.794 (2)	C5—C6	1.356 (3)
K—C8^{iv}	4.086 (3)	C6—C1	1.463 (3)
K—C9^{iv}	3.965 (3)	C7—N5	1.389 (3)
K—C10^{iv}	3.577 (3)	C7—C8	1.383 (3)
K—C11^{iv}	3.290 (3)	C7—C12	1.397 (3)
K—C12^{iv}	3.403 (3)	C8—C9	1.389 (4)
O1—N1	1.225 (2)	C10—C9	1.394 (3)
O3—N2	1.230 (3)	C11—C10	1.378 (4)
N1—O2	1.236 (2)	C12—C11	1.404 (3)
N1—C2	1.439 (3)	C12—C13	1.436 (3)
N2—O4	1.233 (3)	C13—C14	1.396 (4)
N2—C4	1.428 (3)	C13—C18	1.418 (3)
N3—C6	1.455 (3)	C15—C14	1.364 (4)
N3—O5	1.227 (3)	C15—C16	1.386 (4)
N3—O6	1.220 (3)	C16—C17	1.384 (3)
N4—C1	1.303 (3)	C18—C17	1.385 (3)
O1—N1—O2	120.9 (2)	N3—C6—C1	119.9 (2)
O1—N1—C2	120.7 (2)	N3—C6—C5	116.7 (2)
O2—N1—C2	118.3 (2)	C5—C6—C1	123.1 (2)
O3—N2—O4	122.3 (2)	N5—C7—C8	128.0 (2)
O3—N2—C4	119.1 (2)	C12—C7—N5	108.9 (2)
O4—N2—C4	118.6 (2)	C12—C7—C8	123.1 (2)
O5—N3—O6	123.7 (2)	C7—C8—C9	117.2 (2)
C6—N3—O5	117.7 (2)	C8—C9—C10	120.9 (2)
C6—N3—O6	118.5 (2)	C11—C10—C9	121.3 (2)
N5—N4—C1	116.6 (2)	C12—C11—C10	118.9 (2)
N4—N5—C18	127.8 (2)	C7—C12—C11	118.6 (2)
C7—N5—N4	119.3 (2)	C7—C12—C13	107.1 (2)
C7—N5—C18	109.1 (2)	C13—C12—C11	134.4 (2)
N4—C1—C2	121.0 (2)	C12—C13—C14	134.3 (2)
N4—C1—C6	128.1 (2)	C12—C13—C18	107.2 (2)

C6—C1—C2	110.7 (2)	C18—C13—C14	118.5 (2)
N1—C2—C1	122.1 (2)	C13—C14—C15	119.9 (2)
N1—C2—C3	115.7 (2)	C16—C15—C14	120.8 (3)
C1—C2—C3	122.2 (2)	C15—C16—C17	121.5 (2)
C2—C3—C4	119.9 (2)	C18—C17—C16	117.9 (2)
N2—C4—C3	119.3 (2)	N5—C18—C17	130.9 (2)
N2—C4—C5	120.2 (2)	C13—C18—N5	107.7 (2)
C5—C4—C3	120.0 (2)	C13—C18—C17	121.4 (2)
C6—C5—C4	118.9 (2)		
C1—C2—C3—C4	4.9 (1)	C4—C5—C6—C1	−9.6 (1)
C2—C3—C4—C5	11.8 (1)	C5—C6—C1—C2	23.8 (1)
C3—C2—C1—C6	−21.2 (1)	C6—C5—C4—C3	−9.5 (1)

Symmetry codes: (i) $-x, -y, -z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$.

All H atoms were placed in calculated positions on the corresponding C atoms (C—H = 1.00 Å) and were not refined. The U_{iso} of each H atom was assigned as equal to the U_{eq} of the attached C atom plus 0.01. The ω-scan width was $(1.10 + 0.35\tan\theta)°$ with a θ-scan rate of 0.82–4.12° min^{-1}. The scan angle was extended 25% on each side of each peak for background measurement. Refinement was by full-matrix least-squares methods. Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *NRCVAX, ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *NRCVAX TABLES* and *NRCVAX UTILITY*.

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