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The Crystal Structure of Guanidinium Dipicrylaminate, $[C(NH_2)_3]^+[\{C_6H_2(NO_2)_3\}_2.N]^-$

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The crystal structure of guanidinium dipicrylaminate has been determined and the data refined by least-squares calculations to an R of 0·091. In the crystal, dipicrylaminate and guanidinium ions co-exist linked by Coulombic and van der Waals forces. The aromatic rings in the dipicrylaminate anion are in planes nearly normal to each other, the NO_2 groups being rotated out of these planes by angles ranging from 3·6 to 28·6°. The guanidinium cation is nearly planar.

Introduction

The present investigation was undertaken to determine the stereochemistry and dimensions of the dipicrylaminate anion.

Crystal data

Orthorhombic, $a=19{\cdot}46\ (3)$, $b=20{\cdot}56\ (3)$, $c=9{\cdot}88\ (2)$ Å; $D_{obs}=1{\cdot}70$, $D_{cal}=1{\cdot}67$ g cm^{-3}; $Z=8$; space group *Pbca*. μ for Cu $K\alpha$ ($\lambda=1{\cdot}542$ Å) = 14·1 cm^{-1}.

Table 1. *Atomic parameters*

(*a*) Positional parameters and their e.s.d.'s ($\times 10^4$)

	x/a	*y/b*	*z/c*
Guanidinium cation			
C(13)	3869 (6)	1209 (5)	242 (18)
N(8)	3479 (6)	924 (6)	1244 (15)
N(9)	3856 (6)	1859 (5)	58 (15)
N(10)	4294 (5)	848 (5)	−502 (14)
Dipicrylaminate anion			
C(1)	1438 (5)	−688 (5)	277 (15)
C(2)	877 (6)	−424 (5)	962 (16)
C(3)	746 (5)	234 (4)	841 (15)
C(4)	1166 (6)	684 (4)	22 (15)
C(5)	1767 (6)	364 (5)	−589 (15)
C(6)	1902 (6)	−305 (4)	−494 (15)
C(7)	1036 (5)	1902 (4)	−249 (14)
C(8)	1512 (5)	2262 (5)	676 (15)
C(9)	1578 (6)	2912 (5)	771 (15)
C(10)	1147 (6)	3316 (5)	−48 (16)
C(11)	680 (6)	3027 (5)	−1011 (16)
C(12)	647 (5)	2363 (5)	−1091 (15)
O(1)	1197 (5)	−1724 (4)	1109 (13)
O(2)	2021 (5)	−1639 (4)	−400 (13)
O(3)	2273 (5)	1349 (4)	−1272 (12)
O(4)	2684 (5)	446 (4)	−2052 (13)
O(5)	−189 (4)	84 (4)	2274 (11)
O(6)	−19 (4)	1065 (3)	1544 (11)
O(7)	231 (4)	1507 (4)	−2470 (11)
O(8)	−183 (4)	2478 (4)	−2756 (12)
O(9)	1560 (5)	4274 (4)	895 (12)
O(10)	816 (5)	4364 (4)	−704 (12)
O(11)	2529 (4)	2144 (4)	1900 (11)
O(12)	1812 (5)	1339 (4)	1970 (11)
N(1)	1568 (5)	−1397 (5)	303 (15)
N(2)	2268 (5)	743 (4)	−1394 (13)
N(3)	147 (4)	491 (4)	1622 (12)
N(4)	948 (5)	1274 (4)	−301 (13)
N(5)	207 (5)	2100 (4)	−2183 (13)
N(6)	1185 (5)	4009 (4)	32 (14)
N(7)	1983 (5)	1880 (4)	1567 (12)

Table 1 (*cont.*)

(*b*) Thermal parameters and their e.s.d.'s ($\times 10^4$)

$T=\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)]$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Guanidinium cation						
C(13)	26 (4)	15 (3)	76 (36)	4 (3)	−4 (9)	1 (7)
N(8)	34 (4)	38 (4)	95 (28)	5 (3)	19 (8)	29 (8)
N(9)	39 (4)	24 (3)	87 (28)	−3 (3)	2 (8)	−7 (7)
N(10)	36 (4)	20 (3)	93 (27)	6 (3)	1 (8)	−4 (7)
Dipicrylaminate anion						
C(1)	20 (3)	12 (2)	31 (29)	1 (2)	−15 (7)	0 (6)
C(2)	23 (3)	13 (3)	44 (29)	1 (2)	−11 (8)	−9 (6)
C(3)	19 (3)	9 (2)	54 (29)	−2 (2)	−7 (7)	−2 (6)
C(4)	22 (3)	11 (2)	31 (27)	0 (2)	−28 (8)	−4 (6)
C(5)	20 (3)	21 (3)	2 (27)	−3 (2)	−7 (7)	−3 (7)
C(6)	27 (4)	12 (2)	9 (27)	−7 (2)	−20 (7)	0 (6)
C(7)	18 (3)	10 (2)	21 (28)	0 (2)	14 (7)	3 (6)
C(8)	18 (3)	14 (3)	19 (28)	3 (2)	5 (7)	14 (6)
C(9)	17 (3)	19 (3)	6 (27)	−2 (2)	16 (7)	5 (7)
C(10)	22 (3)	16 (3)	27 (29)	1 (2)	10 (8)	5 (7)
C(11)	22 (4)	13 (2)	58 (30)	0 (2)	19 (8)	−8 (7)
C(12)	15 (3)	17 (3)	40 (31)	−1 (2)	2 (7)	6 (7)
O(1)	49 (4)	19 (2)	124 (24)	6 (2)	27 (7)	4 (6)
O(2)	36 (3)	24 (2)	155 (25)	10 (2)	35 (7)	−15 (6)
O(3)	39 (3)	26 (2)	82 (24)	−14 (2)	5 (7)	7 (6)
O(4)	32 (3)	32 (2)	125 (25)	1 (2)	21 (7)	10 (6)
O(5)	24 (3)	25 (2)	69 (21)	−2 (2)	8 (6)	−1 (6)
O(6)	31 (3)	14 (2)	113 (24)	5 (2)	−8 (6)	−6 (5)
O(7)	34 (3)	19 (2)	52 (20)	−5 (2)	−3 (6)	−3 (5)
O(8)	33 (3)	21 (2)	70 (26)	−4 (2)	−29 (7)	7 (5)
O(9)	39 (3)	19 (2)	99 (23)	−1 (2)	−19 (6)	−12 (6)
O(10)	42 (3)	15 (2)	117 (24)	0 (2)	−22 (7)	4 (5)
O(11)	30 (3)	27 (2)	64 (22)	−1 (2)	−16 (6)	8 (5)
O(12)	43 (3)	16 (2)	59 (21)	0 (2)	−17 (7)	2 (5)
N(1)	32 (3)	15 (3)	113 (29)	2 (2)	6 (8)	18 (7)
N(2)	26 (3)	23 (3)	62 (25)	−7 (2)	−5 (7)	22 (6)
N(3)	20 (3)	11 (2)	56 (24)	−2 (2)	−11 (6)	−12 (5)
N(4)	28 (3)	16 (2)	41 (25)	−2 (2)	−8 (7)	5 (6)
N(5)	22 (3)	16 (2)	61 (23)	−2 (2)	−2 (6)	6 (6)
N(6)	24 (3)	14 (2)	78 (25)	−5 (2)	−4 (7)	−11 (6)
N(7)	23 (3)	16 (2)	39 (25)	1 (2)	−3 (6)	−3 (6)

1300 independent reflexions were collected by Weissenberg photography around the [001] needle axis with Cu $K\alpha$ radiation; their intensities were estimated visually and brought to an absolute scale by statistical methods.

Structure determination and refinement

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). 311 reflexions were chosen with $E \geq 1{\cdot}5$. The program automatically chose the phases of three origin-defining reflexions and assigned phases to two other reflexions based on maximum and minimum probability considerations. Three reflexions were assigned symbols and the program generated eight sets of phases with absolute figures of merit ranging between 0·984 and 0·640. The first E map for which the figure of merit was 0·984 revealed the complete structure and gave an R of 0·30. Full-matrix least-squares analysis with the program *ORFLS* (Busing, Martin & Levy, 1962), unit weights for the observed reflexions, and anisotropic temperature factors for the heavy atoms, brought R down to 0·091. An extinction correction was also applied in the last stages of refinement (Zachariasen, 1967). Attempts were made to locate the hydrogen atoms from a difference map but their positions could not be precisely determined; the values are not reported. For the same reason, contributions of the hydrogen atoms are not included in the calculated structure factors (Table 2).

Table 2. *Bond lengths and angles*

(*a*) Bond lengths and their e.s.d.'s

Guanidinium cation			
C(13)–N(8)	1·38 (2) Å	C(13)–N(9)	1·35 (2) Å
C(13)–N(10)	1·33 (2)		
Dipicrylaminate anion			
C(1)–C(2)	1·39 (2)	C(7)—C(8)	1·49 (2)
C(2)–C(3)	1·38 (2)	C(8)—C(9)	1·34 (2)
C(3)–C(4)	1·47 (2)	C(9)—C(10)	1·43 (2)
C(4)–C(5)	1·47 (2)	C(10)–C(11)	1·44 (2)
C(5)–C(6)	1·40 (2)	C(11)–C(12)	1·37 (2)
C(6)–C(1)	1·42 (2)	C(12)–C(7)	1·47 (2)
C(4)–N(4)	1·32 (1)	C(7)—N(4)	1·30 (1)
C(1)–N(1)	1·48 (2)	C(12)–N(5)	1·48 (1)
N(1)–O(1)	1·26 (1)	N(5)—O(7)	1·25 (1)
N(1)–O(2)	1·23 (1)	N(5)—O(8)	1·22 (1)
C(5)–N(2)	1·48 (2)	C(10)–N(6)	1·43 (2)
N(2)–O(3)	1·25 (1)	N(6)—O(9)	1·25 (1)
N(2)–O(4)	1·20 (1)	N(6)—O(10)	1·25 (1)
C(3)–N(3)	1·49 (1)	C(8)—N(7)	1·49 (1)
N(3)–O(5)	1·24 (1)	N(7)—O(11)	1·23 (1)
N(3)–O(6)	1·23 (1)	N(7)—O(12)	1·23 (1)

Results

The numbering scheme is given in Fig. 1. The positional and thermal parameters are given in Table 1.* Bond lengths and angles are in Table 2 and interatomic contacts up to 3·3 Å in Table 3. Equations to the least-squares planes through the dipicrylaminate and guanidinium ions and deviations of atoms from these planes are in Table 4.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30837 (20 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2 (*cont.*)

(*b*) Bond angles and their e.s.d.'s

Guanidinium cation			
N(8)–C(13)–N(9)	120·5 (0·9)°	N(9)–C(13)–N(10)	119·3 (1·0)°
N(8)–C(13)–N(10)	120·1 (0·9)		
Dipicrylaminate anion			
C(1)–C(2)–C(3)	118·9 (0·9)	C(7)—C(8)—C(9)	126·3 (0·9)
C(2)–C(3)–C(4)	124·0 (0·9)	C(8)—C(9)—C(10)	118·7 (0·9)
C(3)–C(4)–C(5)	112·5 (1·0)	C(9)—C(10)–C(11)	120·2 (0·9)
C(4)–C(5)–C(6)	124·0 (0·9)	C(10)–C(11)–C(12)	118·6 (1·0)
C(5)–C(6)–C(1)	117·4 (1·0)	C(11)–C(12)–C(7)	125·8 (0·9)
C(6)–C(1)–C(2)	122·9 (1·0)	C(12)–C(7)—C(8)	110·2 (1·0)
C(4)–N(4)–C(7)	148·9 (1·0)	C(8)—C(7)—N(4)	126·4 (0·9)
C(3)–C(4)–N(4)	121·9 (0·9)	C(12)–C(7)—N(4)	123·3 (1·0)
C(5)–C(4)–N(4)	124·4 (0·9)	C(9)—C(8)—N(7)	115·0 (1·0)
C(2)–C(1)–N(1)	120·6 (0·9)	C(7)—C(8)—N(7)	118·7 (1·1)
C(6)–C(1)–N(1)	116·4 (1·0)	C(8)—N(7)—O(11)	117·0 (1·0)
C(1)–N(1)–O(1)	115·7 (1·0)	C(8)—N(7)—O(12)	120·0 (0·9)
C(1)–N(1)–O(2)	120·8 (1·0)	O(11)–N(7)—O(12)	122·9 (0·9)
O(1)–N(1)–O(2)	123·4 (0·9)	C(9)—C(10)–N(6)	121·0 (1·0)
C(2)–C(3)–N(3)	116·4 (1·0)	C(11)–C(10)–N(6)	118·7 (1·1)
C(4)–C(3)–N(3)	119·6 (1·0)	C(10)–N(6)—O(9)	120·3 (1·0)
C(3)–N(3)–O(5)	116·2 (1·0)	C(10)–N(6)—O(10)	121·1 (1·0)
C(3)–N(3)–O(6)	120·8 (1·0)	O(9)—N(6)—O(10)	118·4 (0·9)
O(5)–N(3)–O(6)	122·8 (0·9)	C(11)–C(12)–N(5)	115·7 (1·1)
C(4)–C(5)–N(2)	120·5 (1·0)	C(7)—C(12)–N(5)	118·3 (1·0)
C(6)–C(5)–N(2)	115·4 (1·0)	C(12)–N(5)—O(7)	119·9 (1·0)
C(5)–N(2)–O(3)	118·6 (1·0)	C(12)–N(5)—O(8)	117·7 (1·0)
C(5)–N(2)–O(4)	117·7 (1·0)	O(7)—N(5)—O(8)	122·5 (0·9)
O(3)–N(2)–O(4)	123·4 (0·9)		

Table 3. *Intermolecular contacts (up to 3·3 Å)*

C(1)····O(4^{ii})	3·18 Å	O(2)····O(11^{viii})	2·99 Å
C(2)····N(3^{iii})	3·24	O(4)····O(9^{vi})	3·04
C(2)····O(6^{iii})	3·26	O(5)····O(10^{v})	3·02
C(9)····O(2^{iv})	3·10	O(5)····O(7^{iii})	3·28
C(10)···O(7^{v})	3·13	O(6)····O(8^{v})	3·09
C(10)···O(12^{vi})	3·25	O(6)····O(10^{v})	3·29
O(1)····O(8^{iii})	2·99	O(7)····N(6^{vi})	3·26
O(1)····N(5^{iii})	3·03	N(2)····O(9^{vi})	3·01
O(1)····N(9^{vii})	3·09	N(3)····O(10^{v})	2·96
O(1)····O(7^{iii})	3·12	N(10)···O(10^{vii})	3·07
N(10)···O(7^{ix})	3·03	N(10)···O(10^{i})	3·22
N(9)····O(8^{ix})	3·21	N(8)····O(11)	3·18
N(9)····O(11)	3·20		

Symmetry code

(i)	$0·5+x\ 0·5-y\ -z$	(vi)	$x\ 0·5-y\ -0·5+z$
(ii)	$0·5-x\ -y\ 0·5+z$	(vii)	$0·5-x\ -0·5+y\ z$
(iii)	$-x\ -y\ -z$	(viii)	$0·5-x\ -y\ -0·5+z$
(iv)	$0·5-x\ 0·5+y\ z$	(ix)	$0·5+x\ y\ -0·5-z$
(v)	$x\ 0·5-y\ 0·5+z$		

Table 4. *Least-squares planes and deviations of atoms from the planes*

Plane		Deviation	Plane		Deviation
(*A*)	C(1)	−0·021 Å	(*B*)	C(7)	0·018 Å
	C(2)	0·013		C(8)	0·0
	C(3)	0·011		C(9)	−0·018
	C(4)	−0·026		C(10)	0·020
	C(5)	0·020		C(11)	−0·001
	C(6)	0·003		C(12)	−0·018
	*N(1)	−0·114		*N(5)	−0·163
	*O(1)	0·011		*O(7)	−0·402
	*O(2)	−0·273		*O(8)	−0·013
	*N(2)	0·057		*N(6)	0·030
	*O(3)	0·379		*O(9)	0·108
	*O(4)	−0·125		*O(10)	0·038
	*N(3)	0·078		*N(7)	−0·045
	*O(5)	0·090		*O(11)	−0·569
	*O(6)	0·043		*O(12)	0·466
	*N(4)	−0·309		*N(4)	0·097
	(*A*)–(*B*)	80·2°		(*B*)–(*F*)	11·2°
	(*A*)–(*C*)	8·1		(*B*)–(*G*)	4·4
	(*A*)–(*D*)	15·0		(*B*)–(*H*)	28·6
	(*A*)–(*E*)	3·6			

Guanidinium cation

$0·7363x+0·1251y+0·6649z=6·0347$ Å (*I*)

	Deviation		Deviation
C(13)	−0·021 Å	N(9)	0·007 Å
N(8)	0·007	N(10)	0·007

Angles between planes

(*I*)–(*A*)	13·5°	(*I*)–(*B*)	93·4°

* *Atoms given zero weight in least-squares calculation.*

Crystal and molecular structure

Molecular structure

The bond lengths and angles in the dipicrylaminate anion are similar to the values reported for a number of picrate anions (Divjakovič, Nowacki, Edenharter, Engel, Ribar & Halasi, 1973; Graeber & Morosin, 1974; Thewalt & Bugg, 1972). C(7)–C(8) (1·49 Å) in the aromatic ring is somewhat longer than expected and the stretching may be a consequence of steric hindrance and molecular packing. Comparable distances for C–C in aromatic rings have been reported (Arora & Pant, 1969; Palmer & Palmer, 1969). In the dipicrylaminate anion, all the NO_2 groups are twisted out of the planes of their aromatic rings by angles ranging from 3·6° to 28·6° (Table 4). The planes of the two aromatic rings make an angle of 80·2° with each other. The guanidinium cation is nearly planar and has similar dimensions to those reported by other workers (Bryden, 1957; Doll & Grison, 1948; Okaya & Pepinsky, 1957).

Crystal structure

The crystal structure is characterized by high packing density. There are seven close contacts (3·03, 3·07, 3·09, 3·18, 3·20, 3·21 and 3·22 Å) linking a guanidinium cation with the dipicrylaminate anion. As no hydrogen atoms were located it is not possible to decide if any

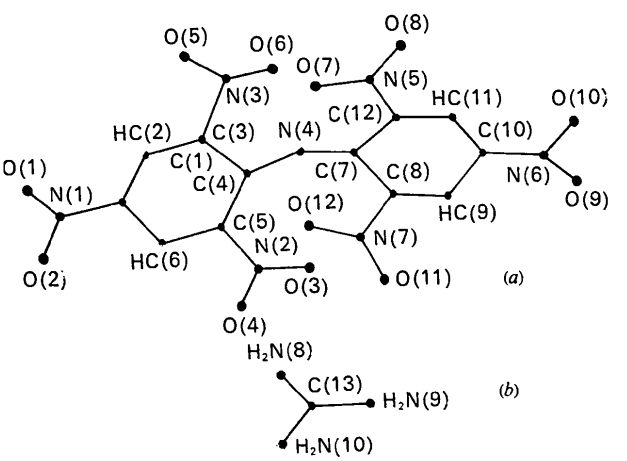

Fig. 1. (a) Dipicrylaminate anion. (b) Guanidinium cation.

Table 4 (*cont.*)

Dipicrylaminate anion

	Equation	Plane
C(1) to C(6)	$0·5582x+0·1753y+0·8109z=\ 1·5573$ Å	(*A*)
C(7) to C(12)	$-0·7144x+0·0057y+0·6997z=-1·6080$	(*B*)
N(1), O(1) and O(2)	$0·6639x+0·1538y+0·7317z=\ 1·8043$	(*C*)
N(2), O(3) and O(4)	$0·5847x-0·0831y+0·8070z=\ 1·3417$	(*D*)
N(3), O(5) and O(6)	$0·5446x+0·2018y+0·8141z=\ 1·6639$	(*E*)
N(5), O(7) and O(8)	$-0·7027x-0·1865y+0·6866z=\ 2·5688$	(*F*)
N(6), O(9) and O(10)	$-0·7392x-0·0594y+0·6708z=-2·1737$	(*G*)
N(7), O(11) and O(12)	$-0·4579x+0·4184y+0·7844z=\ 1·0634$	(*H*)

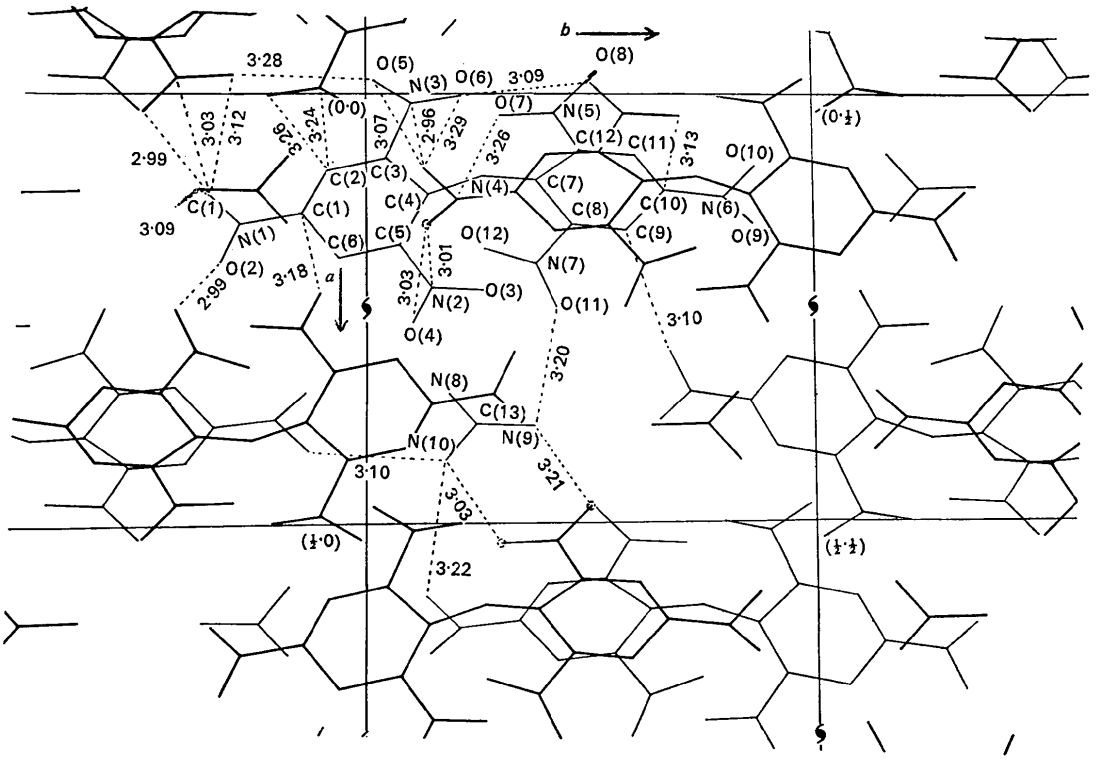

Fig. 2. Crystal structure viewed down [001].

of these contacts represents a weak hydrogen bond. As Table 3 shows, none of the intermolecular contacts is shorter than 2·96 Å. If the sum of the van der Waals radii for the atoms involved in these linkages is considered (Pauling, 1960), the contacts are longer than the normal van der Waals values. The dipicrylaminate and guanidinium ions may, therefore, be regarded as co-existing in the structure, linked by Coulombic and van der Waals forces.

A view of the crystal structure down [001] is given in Fig. 2. In the crystal, the dipicrylaminate anions are stacked in vertical columns spiralling around [001], as a consequence of the screw-axis symmetry operation. The two aromatic rings of this anion, with a dihedral angle of 80·2°, lie nearly in the (402), (40$\bar{2}$) planes, the angle between the latter being 89·1°. The guanidinium ion is also roughly in the same planes (Table 4).

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