Crystal Structure of Dipotassium cis-Hexacyanobutenediide and the Electronic Structure of the Anion

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Abstract: Dipotassium cis-hexacyanobutenediide, $K_2((CN)_2CC(CN)C(CN)C(CN)_2)$, crystallizes in the space group $C2/c$ with $a = 20.08$, $b = 7.42$, $c = 17.36$ Å and $\beta = 117.8°$. There are eight formula units in the unit cell. Data were collected on a three-circle manual diffractometer with Cu Kα radiation. The structure was solved by Patterson and heavy-atom Fourier methods and was refined by full-matrix least squares, based on 1767 unique observed reflections, to a final conventional R index of 0.072. The anions lie approximately parallel to the **a**, **c** plane and stack along **b**, which is the needle axis. Each potassium ion is surrounded by seven terminal nitrogen atoms from six different anions and is enclosed between the planes of anions. Observed bond lengths are in agreement with the predictions of molecular orbital theory, and the bond angles and average values of the torsion angles agree with those expected from extended molecular orbital calculations. The relatively small deviation of the anion from the C_2 symmetry that is predicted by the calculations can be attributed to interactions with neighboring potassium ions.

Hexacyanobutadiene (HCBD) is a strong π acid which forms charge-transfer complexes with aromatic compounds and is readily reduced to the ion radical and further to the dianion. Although a planar structure for this compound would be impossibly strained, its ultraviolet spectrum indicates that the entire molecule is conjugated.[2] The structures of related compounds, for example, butadiene,[3] tetracyanoethylene,[4] and the hexacyanoisobutylene dianion,[5] provide models for comparison with HCBD or a derivative.

Since good crystals of the potassium salt of the cis dianion (K_2HCBD) were available, the determination of its structure was undertaken. We found the dianion to be twisted about the three bonds in the central four-carbon chain, the internal angles being opened in such a manner as to minimize crowding (Figure 1[6]).

We discuss first the details of the structure determination of K_2HCBD, and then the general packing features and environment about the potassium ions, the geometry of the anion, and the predictions made about anion geometry from molecular orbital calculations. Finally we compare features of the anion with those of related species.

Experimental Section

Clear, orange needlelike crystals of dipotassium cis-hexacyanobutenediide were supplied by Dr. O. W. Webster. It had crystallized at 0° at the interface between an ether solution of 1-aminocyclopentadiene and aqueous potassium hydroxide, following the reaction
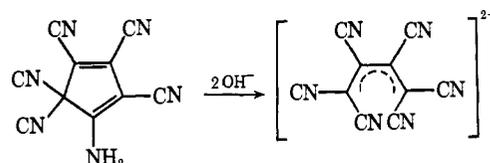
The space group assignment $C2/c$ was determined from the absence of hkl reflections with $(h + k)$ odd and of $h0l$ reflections with l odd on Weissenberg photographs of the $h0l$, $h1l$, and $h2l$ levels, and a precession photograph of the $hk0$ level;[7] the distribution of average E values[8] calculated from the intensity data indicates a center of symmetry.

Measurements on precession photographs and centering of a number of reflections on a Picker manual diffractometer led to the following lattice parameters:[9] $a = 20.077$ (7), $b = 7.421$ (10), $c = 17.355$ (7) Å and $\beta = 117.8$ (1)°. Cu Kα radiation, λ 1.5418 Å, was used for determination of lattice parameters as well as for data collection. The cell volume is 2288.0 Å^3. The calculated density for $Z = 8$ is 1.639 g cm^{-3}; the approximate density measured by flotation was 1.65 (5) g cm^{-3}.

Intensities were measured to 131° in 2θ with a small needle-shaped crystal of cross section 0.06×0.12 mm. Because of the gradual deterioration of these crystals under exposure to X-rays, background intensities were measured only infrequently, and these measurements were used to construct a smooth curve of background intensity as a function of 2θ. The manual diffractometer, with a moving-crystal–moving-counter technique and θ–2θ scans, was used for data collection.

To reduce intensities (after subtraction of background from observed intensity) to relative F^2 values, a correlation factor, determined from the daily monitoring of the 6,0,0 peak, and the Lorentz-polarization correction were applied. No absorption or secondary extinction corrections were made.

Observed and calculated structure factors for the 1985 unique reflections which complete the sphere of reflection to $2\theta = 131°$ (($\sin \theta$)/$\lambda = 0.59$) are listed in Table I.[10]

(1) (a) The authors gratefully acknowledge National Science Foundation Grants No. GP10949 and G20207 and National Institutes of Health Grant No. GM13468, which supported this research; (b) Cornell University.

(2) O. W. Webster, *J. Amer. Chem. Soc.*, **86**, 2898 (1964).

(3) (a) A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958); (b) W. Haugen and M. Traetteberg, *ibid.*, **20**, 1726 (1966); (c) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1968).

(4) (a) D. A. Bekoe and K. N. Trueblood, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **113**, 1 (1960); (b) D. A. Bekoe and K. N. Trueblood, Abstracts of the Meeting of the American Crystallographic Association, Bozeman, Montana, 1964, Paper No. J12; (c) H. Hope, *Acta Chem. Scand.*, **22**, 1057 (1968).

(5) D. A. Bekoe, P. K. Gantzel, and K. N. Trueblood, *Acta Crystallogr.*, **22**, 657 (1967).

(6) These drawings were made with the aid of the ORTEP thermal ellipsoid program for the Calcomp plotter written by C. S. Johnson.
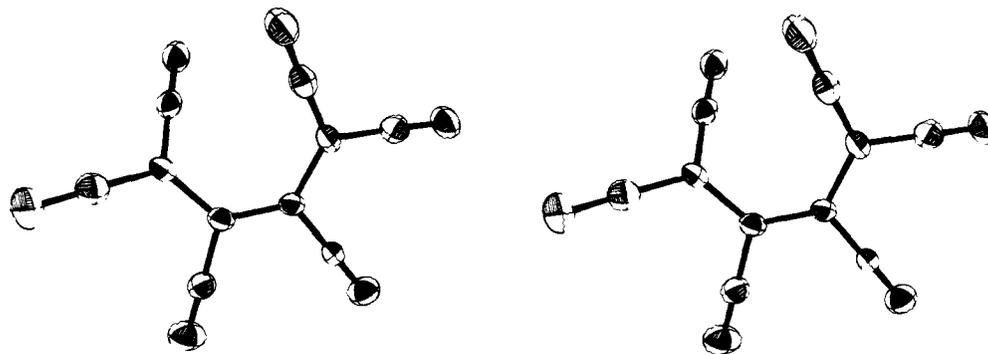
(7) "International Tables for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1965, p 101.

(8) I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr.*, **19**, 713 (1965).

(9) Approximate esd's, shown in parentheses, are right justified to the least significant digit of the preceding number.

(10) Table I, and a more detailed description of the structure solution and refinement, will appear following these pages in the microfilm

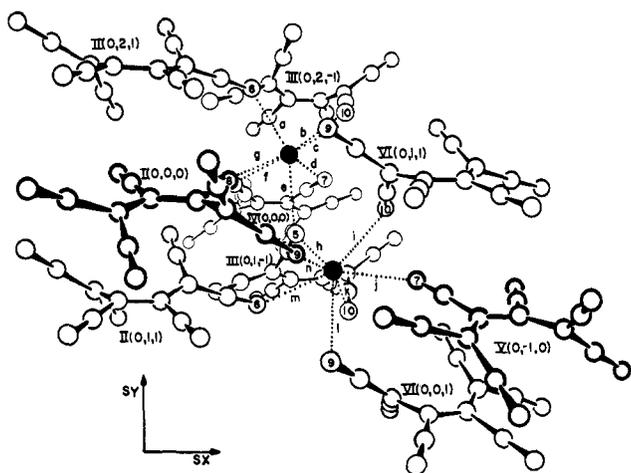Figure 1. Stereoscopic view of the anion cis-HCBD^{2-}.

Figure 2. Packing of anions around the two nonequivalent potassium ions viewed down c*. Equivalent positions and unit translations for the anions are labeled.[14] The drawing is adapted from an ORTEP[6] plot centered at the III (0, 1, −1) anion. The shortness of the viewing distance exaggerates the perspective. Most of the nitrogen atoms referred to in Table IV are numbered for easy reference. SX and SY are orthogonal coordinates parallel to a and b, respectively. The lettered contacts are identified in Table IV.

Structure Determination and Refinement

The positions of the two independent potassium ions were readily deduced from a three-dimensional sharpened Patterson synthesis. The other 16 atoms in the asymmetric unit were located with three-dimensional electron-density maps, and all atoms were refined by full-matrix least squares[11,12] with anisotropic temperature factors, to a final discrepancy index, R, of 0.072 for the 1767 reflections for which $|F_{obsd}|$ is greater than 3σ-(F).[13] In the final refinement cycle,[12,13] the average parameter shifts were about 0.05 esd of position, the approximate esd of the electron density was 0.14 e Å^{-3}, and the unweighted R index including the 218 unobserved reflections at $|F_{obsd}|_{min}/\sqrt{3}$ was 0.079. Final atomic parameters are listed in Table II.

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(11) The program used for least-squares refinement (P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, FMLS1, unpublished) minimizes $\Sigma w(|\Delta F|)^2$, where w is $1/\sigma^2(F)$.

(12) Scattering factors for K$^+$, C(valence) and N^0 were used throughout: see reference 7, Vol. III, 1962, p 202.

(13) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968, p 457, equation H.14.
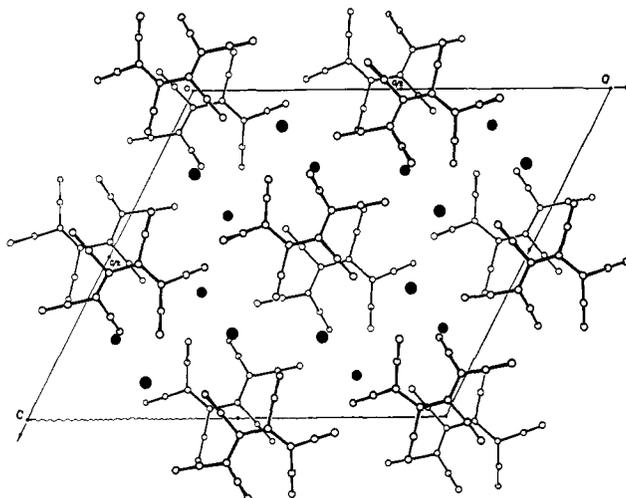

Figure 3. The unit cell viewed down b. The black dots represent the potassium ions.

General Packing Features and Potassium Ion Environment

There are eight anions and eight pairs of nonequivalent potassium ions in the unit cell. The anions are arranged in approximately planar layers, stacked along b (Figures 2 and 3). The potassium ions are enclosed between these planes, their positions being fixed by short contacts with the nitrogen atoms of the cyano groups. The twist of the terminal cyano groups permits an interleaving of the anion planes, and consequently cages are formed by the layers. Each cation is surrounded by such a cage, formed by seven different nitrogen atoms. All the K–N contacts smaller than 4.0 Å are listed in Table III. The corresponding distances are labeled in Figure 2.

Nine of these distances are less than the sum of the van der Waals' radii for N and K$^+$ atoms (3.1 Å, taking the approximate radii to be 1.7, 1.6, and 1.5 Å for C, N, and K$^+$, respectively). Although the environments of the two potassium ions are not alike, the average K–N distances (Table III) are the same for both, within experimental error. The closest K–K distance is 4.17 Å, between K(1), position I, and K(2), position I (0, 1, 0).[14]

(14) The equivalent positions of the space group $C2/c$ are indicated by Roman numerals as follows: I, x, y, z; II, $-x, -y, -z$; III, $x, -y$, $1/2 + z$; IV, $-x, y, 1/2 - z$; V, $1/2 + x, 1/2 + y, z$; VI, $1/2 - x, 1/2 - y$, $-z$; VII, $1/2 + x, 1/2 - y, 1/2 + z$; VIII, $1/2 - x, 1/2 + y, 1/2 - z$. Unit translations along unit cell axes are indicated in parentheses. Thus K(1), I (0, 1, 0) is at $x, 1 + y, z$. Position I is given in Table II.

Table II. Final Atomic Coordinates (with esd's)[a]

Atom	x	y	z
K(1)	0.10935 (7)	0.92585 (18)	0.25771 (7)
K(2)	0.23686 (6)	0.37968 (18)	0.38268 (7)
C(1)	0.0201 (3)	0.6685 (7)	0.6248 (3)
C(2)	0.0199 (3)	0.7223 (7)	0.5448 (3)
C(3)	0.0799 (3)	0.7160 (7)	0.5250 (3)
C(4)	0.1573 (3)	0.6852 (8)	0.5861 (3)
C(5)	0.0726 (3)	0.5464 (7)	0.6845 (3)
C(6)	−0.0410 (3)	0.7204 (8)	0.6397 (3)
C(7)	−0.0508 (3)	0.7906 (8)	0.4778 (3)
C(8)	0.0630 (3)	0.7625 (8)	0.4378 (3)
C(9)	0.2034 (3)	0.5824 (8)	0.5623 (3)
C(10)	0.1884 (3)	0.7649 (8)	0.6680 (3)
N(5)	0.1134 (2)	0.4454 (7)	0.7344 (3)
N(6)	−0.0915 (2)	0.7654 (8)	0.6503 (3)
N(7)	−0.1071 (3)	0.8427 (7)	0.4250 (3)
N(8)	0.0506 (3)	0.8031 (8)	0.3683 (3)
N(9)	0.2413 (3)	0.4990 (8)	0.5414 (3)
N(10)	0.2117 (2)	0.8391 (7)	0.7347 (3)

			Anisotropic Thermal Parameters[b] ($\times 10^5$)			
Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
K(1)	317 (3)	1135 (23)	346 (4)	−241 (17)	446 (5)	−138 (18)
K(2)	185 (3)	1453 (24)	256 (4)	6 (17)	230 (5)	−110 (19)
C(1)	185 (12)	1073 (100)	225 (16)	−12 (63)	271 (19)	28 (71)
C(2)	160 (12)	955 (95)	159 (16)	46 (62)	141 (20)	−86 (70)
C(3)	182 (13)	1033 (98)	172 (16)	−114 (66)	175 (20)	9 (73)
C(4)	198 (13)	1167 (103)	177 (16)	55 (64)	230 (20)	−27 (71)
C(5)	203 (12)	1006 (102)	275 (17)	−18 (64)	305 (20)	−116 (73)
C(6)	209 (14)	1270 (109)	261 (19)	−31 (73)	206 (24)	281 (82)
C(7)	153 (12)	1341 (107)	188 (16)	−19 (65)	196 (20)	−15 (74)
C(8)	188 (14)	1283 (109)	238 (19)	−111 (69)	190 (23)	−8 (80)
C(9)	228 (15)	1395 (116)	267 (19)	157 (76)	239 (24)	216 (86)
C(10)	146 (13)	1137 (104)	267 (20)	−102 (64)	176 (23)	114 (77)
N(5)	262 (12)	1360 (98)	318 (16)	124 (61)	383 (19)	149 (69)
N(6)	246 (12)	2313 (126)	368 (18)	383 (71)	400 (20)	548 (83)
N(7)	231 (13)	1631 (106)	310 (19)	160 (70)	173 (24)	55 (81)
N(8)	357 (16)	2110 (125)	281 (18)	−521 (78)	326 (24)	−55 (83)
N(9)	284 (14)	2226 (125)	415 (20)	591 (72)	372 (24)	−83 (89)
N(10)	188 (12)	1433 (101)	317 (17)	−101 (62)	209 (21)	−77 (74)

[a] Esd's are in parentheses. [b] The anisotropic thermal parameter is expressed as $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

The angles between K–N vectors are also given in Table III. If the K⁺ ions were surrounded by six instead of seven near contacts, one would expect the
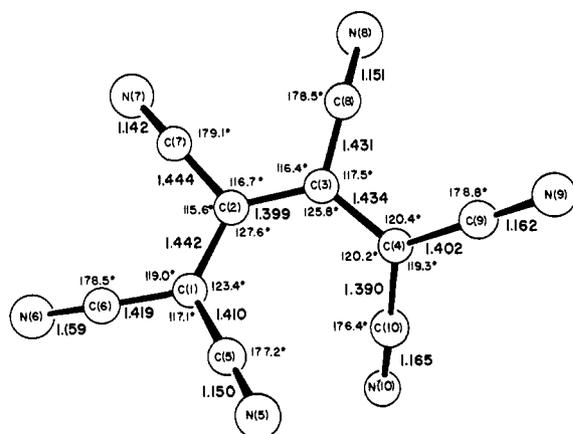

Figure 4. Bond lengths and bond angles in the HCBD²⁻ anion. Average esd's are 0.009 Å for bond lengths and 0.5° for bond angles.

angles subtended by two neighboring nitrogen atoms to average 90°, the octahedral angle. With seven neighbors, the angles are somewhat smaller; most fall between 70 and 85°, within the range from about 65–110°.

The potassium ions are thus enclosed in cages of moderately evenly spaced nitrogen atoms.

Anion Geometry

The HCBD²⁻ anion, in the idealized cis planar geometry, would have impossibly short intramolecular contacts; C(5) and C(10) would be about 1.4 Å apart and N(5) and N(10) would approximately coincide. In the crystal structure, the anion shows (Table IV and Figure 4) considerable deviations from planarity and some distortion of bond angles, which minimize crowding. The terminal cyano groups are twisted about the C(1)–C(2) and C(3)–C(4) bonds of the central four-carbon chain, and the angles C(1)–C(2)–C(3) and C(2)–C(3)–C(4) are enlarged from the sp² angle of 120° to 127.6 and 125.8°, respectively (Figure 4). These distortions lead to minimum nonbonded C–C distances of 2.69, C(7)–C(8); 2.77, C(6)–C(7); 2.95, C(8)–C(9); and 2.96 Å, C(5)–C(10).

Those bonded distances expected to be chemically equivalent are approximately equal. The C(1)–C(2) and C(3)–C(4) distances of 1.44 and 1.43 Å are somewhat shorter than the single bonds commonly observed in conjugated compounds, while the C(2)–C(3) distance of 1.40 Å is appreciably longer than typical double bonds.[15]

(15) J. F. Chiang and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 261

Table III. Short K–N Distances[a,b] and
Angles around Potassium Ions

From ion	Position	To atom	Position	Vector in Figure 2	Distance, Å
K(1)	I (0, 0, 0)	N(5)	III(0, 1, −1)	e	2.79
		N(8)	I(0, 0, 0)	g	2.83
		N(10)	III(0, 2, −1)	b	2.86
		N(6)	II(0, 2, 1)	a	2.91
		N(8)	IV(0, 0, 0)	f	3.06
		N(7)	IV(0, 0, 0)	d	3.21
		N(9)	VI(0, 1, 1)	c	3.42
					Av 3.01
K(2)	I (0, 0, 0)	N(9)	I(0, 0, 0)	n	2.86
		N(7)	V(0, −1, 0)	j	2.88
		N(10)	III(0, 1, −1)	k	2.88
		N(6)	II(0, 1, 1)	m	2.91
		N(5)	III(0, 1, −1)	h	2.92
		N(9)	VI(0, 0, 1)	l	3.05
		N(10)	VI(0, 1, 1)	i	3.40
					Av 2.99

Vectors in Figure 2	Angle, deg	Vectors in Figure 2	Angle, deg
eg	80	nj	104
eb	121	nk	162
ea	151	nm	83
ef	72	nh	110
ed	70	nl	87
ec	104	ni	120
gb	148	jk	84
ga	72	jm	152
gf	76	jh	130
gd	142	jl	83
gc	79	ji	67
ba	82	km	82
bf	132	kh	75
bd	70	kl	78
bc	72	ki	78
af	106	mh	69
ad	138	ml	71
ac	66	mi	132
fd	73	hl	133
fc	155	hi	64
dc	130	li	144

[a] Distances ≤4.0 Å are included. [b] See ref 14.

The nonplanarity of the four-carbon central chain, as well as of each trigonal carbon atom and its three immediate neighbors, is illustrated by the torsion angles and least-squares planes listed in Table IV. The average torsion angles[16] about the C(1)–C(2) and C(3)–C(4) bonds are 18 and 39°, respectively. However, the lack of planarity complicates any consideration of these angles. Because the torsion angle about the C(2)–C(3) bond is about 12°, it seems more meaningful to represent the twisting of the anion by the angles between the least-squares planes of the central four-carbon chain (plane A) and the planes including the terminal groups (planes B and C). These angles are 25 and 46°, respectively; the terminal groups are more severely twisted out of the plane of the four-carbon chain at the C(4) end than at the C(1) end of the anion.

The deviation from C_2 symmetry, observed in the differing torsion angles about the C(1)–C(2) and C(3)–C(4) bonds, is presumably due to the packing arrangement. The cyano nitrogen atoms differ somewhat in the number and nature of their closest interionic neigh-

(1970). A table of –C=C– and =C—C= bond lengths is included in this paper.

(16) The averages of the absolute deviations from 0 and 180° are used to avoid complications with sign conventions.
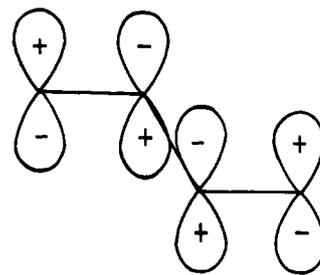
Figure 5. The χ_3 molecular orbital of butadiene.

bors. Each of the six unique nitrogen atoms (Table III) has two potassium ions as near neighbors, and N(9) and N(10) have a third potassium ion each, at a distance of about 3.4 Å. Thus, the potassium ions play a greater role in the environment of the cyano groups at the C(4) end of the four-carbon chain than in that of the rest of the anion.

Analysis of thermal motion[17] in the anion showed that neither the four-carbon central chain nor the ten-carbon frame of the ion, nor in fact the entire ion, can be adequately described as a rigid body. In tetracyanoethylene[4] and the hexacyanoisobutylene anion,[5] treating the carbon framework as a rigid body with wagging terminal nitrogen atoms led to a rather considerable correction to the –C≡N bond lengths. The failure of this kind of analysis for HCBD[2−] may be due to inaccuracies in the thermal parameters because no absorption correction was made.

The Electronic Struture of $C_4(CN)_6{}^{2-}$

Consider first the parent molecule, butadiene (1), and its dianion. The stable geometry[3b] of 1 is s-trans, with

1
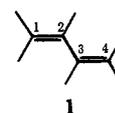
C(1)–C(2) = C(3)–C(4) = 1.344 and C(2)–C(3) = 1.467 Å. Despite many years of work, it is not known if the corresponding s-cis geometry is a potential energy maximum or a local minimum.[18] What is known is that the barrier to torsion about the C(2)–C(3) bond is small (<10 kcal/mol) and that the s-cis geometry is readily populated thermally. The torsional barriers around the C(1)–C(2) and C(3)–C(4) bonds, corresponding to their normal double-bond character, are expected to be large (>40 kcal/mol).

The changes in geometry and torsional barriers as a result of adding two electrons to butadiene are easily anticipated on examination of its molecular orbitals. The difference between the neutral molecule and the dianion is that in the former the third butadiene π orbital, χ_3, is empty, while in the latter it is doubly occupied. χ_3 is C(1)–C(2) and C(3)–C(4) antibonding and C(2)–C(3) bonding (Figure 5). We are led to expect that in the dianion there will be increased C(2)–C(3) bonding, as manifested by a shorter C(2)–C(3) bond and a larger torsional barrier around that bond, and also decreased C(1)–C(2) and C(3)–C(4) bonding, with corresponding

(17) V. Schomaker and K. N. Trueblood, Acta Crystallogr., Sect. B, 24, 63 (1968).

(18) See evidence reviewed by R. Hoffmann, Tetrahedron, 22, 521 (1966).

Table IV. Anion Geometry

	Torsion Angles,[a] deg	
	Atoms	Angle
	C(1)-C(2)-C(3)-C(4)	-12.1
	C(5)-C(1)-C(2)-C(3)	-22.2
	C(6)-C(1)-C(2)-C(3)	166.6
	C(2)-C(3)-C(4)-C(10)	-40.7
	C(2)-C(3)-C(4)-C(9)	142.7

Least-Squares Planes[b,c]						
	A	B	C	D	E	F	G
$10^4 l_1$	0274	3584	-4665	3587	-4665	1132	0508
$10^4 l_2$	9608	7896	-8111	7894	-8111	9246	9714
$10^4 l_3$	2760	4982	3529	4981	3529	3637	2320
d, Å	-7.364	-7.029	0.277	-7.011	0.282	-7.604	-7.006

Deviations, Å $\times 10^3$						
C(1)	-21	46		62			
C(2)	46	-16		0		-0	0
C(3)	-46		-6		0	0	-47
C(4)	20		18		24		0
C(5)		-16		0			
C(6)		-15		0			
C(7)	230					0	
C(8)	-70						0
C(9)			-6		0		
C(10)			-6		0		
N(7)	363						
N(8)	-63						

[a] Only the relative values of angles are significant, since the structure contains pairs of anions related by centers of symmetry. [b] The equation of each plane is in the form $l_1(SX) + l_2(SY) + l_3(SZ) + d = 0$, where SX, SY, and SZ are orthogonal coordinates parallel to **a**, **b**, and **c***. [c] The atoms used to determine the plane are indicated by a boldface distance from the plane.

bond-length increases and smaller torsional barriers. The direction of the changes in every instance counteracts the ground-state preferences. Moreover, the simplest Hückel calculation also indicates that the ground-state trends will be reversed. Thus, in the dianion the C(1)-C(2) bond order is 0.448, while that for C(2)-C(3) is 0.722. We can thus expect that in the dianion of butadiene, the C(2)-C(3) bond will be shorter than the C(1)-C(2) and C(3)-C(4) bonds. Corre-
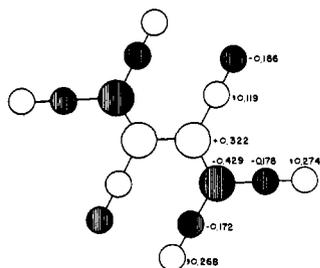

Figure 6. The highest occupied molecular orbital of HCBD[2−].

spondingly, there should be a large torsional barrier around the C(2)-C(3) bond, leading to conformationally fixed cis-trans isomers and smaller torsional barriers around the C(1)-C(2) and C(3)-C(4) bonds. These conclusions are consistent with results of extended Hückel calculations[19] on model butadiene dianions.[20]

(19) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); **40**, 2474, 2480, 2745 (1964), and subsequent papers.
(20) The construction of the correlation diagram for torsion around the C(2)-C(3) bond shows in another way the large barrier in the dianion. See problem 9.6 in E. Heilbronner and H. Bock, "Das HMO-Modell und seine Anwendung," Verlag Chemie, Weinheim/Bergstr., 1968.

We now turn to the theoretical analysis of the hexacyanobutadiene dianion. The π orbitals of this ion are considerably delocalized. The highest occupied molecular orbital in a planar s-trans geometry of the dianion is shown in Figure 6. We are viewing the top lobes of the atomic orbitals; no shading indicates positive sign and shading indicates negative sign, with orbital coefficients indicated. Note that in the central four-carbon skeleton the nodal structure is identical with that in χ_3 of butadiene. We thus would expect qualitatively the same bond-length and torsional barrier changes in $C_4(CN)_6{}^{2-}$ as in $C_4H_6{}^{2-}$. For the hexacyanobutenediide ion, the observed bond distances of C(2)-C(3) = 1.40 and C(1)-C(2) = 1.44, C(3)-C(4) = 1.43 Å, are in accord with expectations.

We now consider the torsion angles. Figure 7 shows an extended Hückel potential energy curve for $\tau_{12} = \tau_{34} = 0$, τ_{23} varied. $\tau_{23} = 180°$ corresponds to a planar s-trans geometry, $\tau_{23} = 0°$ to s-cis. The bond distances used are those found experimentally in the present study. Note the following. (1) The energy rises sharply as τ_{23} approaches 0°. A pure cis geometry would obviously have inadmissably short atom–atom contacts. (2) There is a sizable torsional barrier of approximately 1 eV. (3) The minimum on the s-trans side is not at $\tau_{23} = 180°$.

A study of τ_{12} and τ_{34} showed that the energy changes little as these angles are varied. Since the steric problems on the s-cis side could be avoided by a combination of changes in τ_{12} and τ_{34} with changes in τ_{23}, it became obvious that all angles should be varied simultaneously to locate the true theoretical minima. We turned to an automatic minimum-seeking program which allowed the molecule four degrees of freedom. These were the torsion angles τ_{12}, τ_{23}, and τ_{34}, and the C(1)-C(2)-C(3) angle, α, maintained equal to the C(2)-C(3)-C(4) angle.[21]
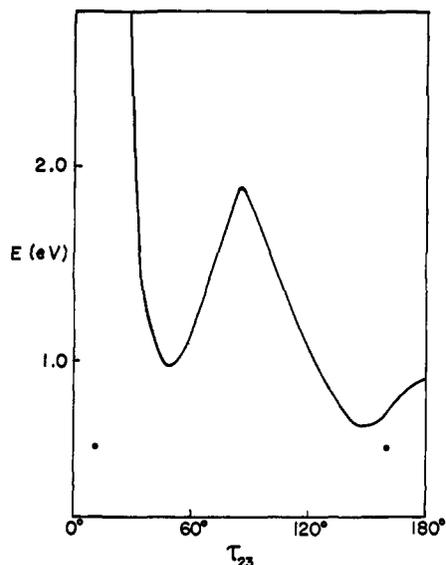
Figure 7. Potential energy curve for twisting a hypothetical planar hexacyanobutadiene around the central bond. $\tau_{23} = 0$ corresponds to s-cis, $\tau_{23} = 180°$ to s-trans. The energy scale is in electron volts relative to an arbitrary zero. The heavy dots are the energies of the two minima located when τ_{12} and τ_{34} were also allowed to vary.

Our calculations homed in on two energy minima. The first corresponds to the crystal structure, and is located at $\alpha = 126.7°$, $\tau_{12} = 31.9°$, $\tau_{23} = 11.6°$, $\tau_{34} = 32.2°$. These angles are estimated to deviate by at most 2° from the true theoretical minimum. The angles obtained from the crystal structure are $\alpha = 126.7°$ (average of two values), $\tau_{12} = 25°$, $\tau_{23} = 12°$, $\tau_{34} = 46°$. The agreement for α and τ_{23} is excellent. The molecule in the crystal deviates somewhat from C_2 symmetry. Our theoretical model, which was not constrained to C_2 symmetry, nevertheless chose a configuration very close to that symmetry.[22] The difference between τ_{12} and τ_{34} in the crystal is evidently due to a packing preference. The experimental average[23] of τ_{12} and τ_{34}, 36°, is near the calculated minimum. The agreement between observed and calculated molecular parameters is thus very good.

Encouraged by this calibration of the theoretical method, we may proceed to predict the structure corresponding to the other minimum, which should be the other hexacyanobutadiene isomer found by Webster.[2] There is apparently no structural information on this species. Allowing once again independent variation of all four degrees of freedom, we find the second minimum at $\alpha = 125.5°$, $\tau_{12} = 21.3°$, $\tau_{23} = 160.0°$, $\tau_{34} = 20.1°$. The symmetry is again very close to C_2. The energies of the s-cis and s-trans minima, both indicated by dots in Figure 7, are within 0.01 eV of each other.[24]

(21) The remaining geometrical parameters were taken from the crystallographic study, except that substituent angles at C(1) and C(4) were idealized to 120°. The CN groups at C(2) and C(3) were placed along the bisector of α.

(22) When our minimization procedure was started at the crystal structure parameters, it moved along a path of uniformly decreasing energy to the minimum quoted in the text.

(23) The average value 36° is that of the angles between the least-squares planes of Table IV, as mentioned earlier. If the four torsion angles of the individual arms at the ends of the anion are averaged, the value is 29°.

(24) Equilibration studies of the disodium salt of hexacyanobutadiene led to a 0.8 kcal/mol (0.03 eV) preference for the trans isomer (ref 2).
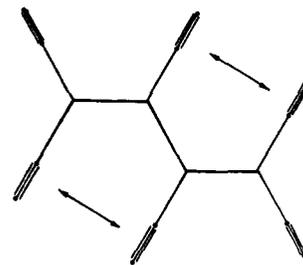

Figure 8. Structural representation of s-trans-hexacyanobutadiene. The arrows indicate potentially short intramolecular distances that will be lengthened by torsion about the C–C bonds of the chain.

The deviation of this second minimum from planarity may at first sight seem surprising. However, although the extreme contacts of the s-cis conformation are absent in a planar s-trans geometry, there would still remain CC and NN contacts of 2.6–2.7 Å between the cyano groups indicated in Figure 8. Combined torsions avoid these short contacts. Our predictions for this structure are supported by the observed torsional angles of 24° in the anion $C(C(CN)_2)_3{}^{2-}$, where a similar steric problem exists.[5] Finally, though the absence of a bond order–bond length curve makes an exact prediction difficult, we would on the basis of the calculated overlap populations in the two minima anticipate that the C(1)–C(2) and C(3)–C(4) bonds should be slightly shorter and the C(2)–C(3) bond slightly longer in the s-trans isomer than in the s-cis.

Discussion

The geometry of the cis-hexacyanobutadiene dianion implies a high degree of delocalization of charge. The C(2)–C(3) bond is much longer, at 1.399 Å, than double bonds observed in related compounds, for example, 1.344 Å in butadiene,[3b] 1.349 Å in 2,3-dimethylbutadiene,[25] and 1.339 Å in tetracyanoethylene.[4c] Lengthened formal double bonds have been found in 1,3,5-cis- and 1,3,5-trans-hexatriene,[26] the central double bonds at 1.362 and 1.368 Å, respectively, being considerably longer than the terminal double bonds at 1.337 Å. The cis compound also is twisted about the central bond by about 10°, and the C—C=C internal angle is opened to 125.9°, compared to 123° in butadiene. These features are remarkably similar to the twist of 12° and average internal angle of 126.7° in HCBD^{2-} (Table IV and Figure 4).

It is interesting to compare HCBD^{2-} with the dianion of hexacyanoisobutylene,[5] HCB^{2-}. The latter anion retained C_3 symmetry in the hydrated calcium salt, while HCBD^{2-} has lost its rotational symmetry in the present structure. In HCB^{2-}, the –C–C– bond distances average 1.425 Å, or about the same as the C(1)–C(2) and C(3)–C(4) distances in HCBD^{2-}, which average 1.438 Å. Some of the –C≡N distances in HCBD^{2-} are long relative to others found in X-ray structure analyses. Such distances typically are reported[4,5,27,28] in the range 1.11–1.15 Å, before correction for thermal motion.

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The observed variations in bond distances, as well as the deviations from planarity, are all consistent with the Hückel molecular orbital picture, which indicates that the highest filled molecular orbital of the dianion makes an antibonding contribution to C(2)–C(3) and to each C≡N bond, and bonding contributions to the other C—C bonds.

Structural Characterization of a 1-Substituted 5-Tetrazolyl(transition metal) Complex Containing Metal–Carbon Bonding. Stereochemistry of the Tetrakis(1-isopropyltetrazol-5-ato)aurate(III) Anion, [Au(CN₄R)₄]⁻ (R = i-C₃H₇)

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Abstract: An X-ray crystallographic study of the salt [As(C₆H₅)₄][Au(CN₄R)₄] (where R = i-C₃H₇), obtained from the reaction of [As(C₆H₅)₄][Au(N₃)₄] with isopropylisonitrile, has not only ascertained the existence of a 1-substituted tetrazol-5-ato–metal complex with a metal–carbon σ-bonded covalent linkage but in addition has provided the detailed stereochemistry of a [Au(CN₄R)₄]⁻ anion. The four tetrazole rings are coordinated in a square-planar arrangement about the central gold(III) with the tetrazole rings oriented such that four rings lie in two mutually perpendicular planes with each pair of trans rings coplanar. The overall symmetry of the entire anion approximately conforms to the S_4-$\bar{4}$ point group with the S_4 improper rotation axis perpendicular to the AuC₄ plane and passing through the gold atom. This sterically most favorable geometry with the isopropyl substituent located at the 1 position of the planar five-membered ring may account for the remarkable stability of the [Au(CN₄R)₄]⁻ anions to various chemical reagents in that the substituent R groups effectively block to a considerable extent the two vacant octahedral-like coordination sites at the Au(III) against chemical attack. The four Au–C bond lengths range from 1.95 (4) to 2.00 (4) Å with the mean value of 1.98 Å corresponding to a covalent single-bond length. The differences among the equivalent C–N and N–N distances of the four tetrazole rings are not significant, and the average values compare favorably with those in other structurally determined tetrazole derivatives for which electron delocalization has been proposed. The [As(C₆H₅)₄][Au(CN₄R)₄] (R = i-C₃H₇) salt crystallizes with two formula species in a monoclinic unit cell of symmetry $P2_1$ and of dimensions $a = 11.07$, $b = 18.66$, $c = 11.36$ Å, $\beta = 104.5°$. The crystal structure was solved by the heavy-atom method and refined by full-matrix, rigid-body, anisotropic–isotropic least squares to an unweighted R_1 value of 6.0% based on 1426 independent absorption-corrected, diffractometry-obtained intensity maxima.

Although many studies of metal complexation with either neutral or anionic unsubstituted and substituted tetrazoles have been reported,[1–12] detailed

stereochemical information concerning the nature of the metal–tetrazole link(s) has only recently become available.

Tetrazolato–metal complexes are formed by the cycloaddition of metal azides with either organic nitriles[8–10] or isonitriles.[8,11] Beck and coworkers[8,9] showed that the former reaction yields 5-substituted tetrazolato–metal complexes in which the metal is nitrogen coordinated.[12] A recently performed X-ray structural investigation of the complex trans-[(C₆H₅)₃P]₂Pd(N₄C-(C₆H₅))₂, which was synthesized by reaction of trans-[(C₆H₅)₃P]₂Pd(N₃)₂ and benzonitrile,[9] showed the tetrazolato ligand to coordinate to the metal through the nitrogen at position 2.[13] On the other hand, it was suggested that the N(1) nitrogen atom can function as

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