

Fig. 5. (a) Packing of the phenyl ring atoms around the perchlorate ion, as viewed along the  $b^*$  axis. (b) Packing of the methyl groups around the perchlorate ion, as viewed along the  $c$  axis.

- ROLLETT, J. S. & DAVIES, D. R. (1955). *Acta Cryst.* **8**, 125.  
 SCHUYTEN, M. C. (1898). *J. Chem. Soc. Abstracts*, Part I, **74**, 452.  
 SCHUYTEN, M. C. (1900). *J. Chem. Soc. Abstracts*, Part I, **78**, 57.  
 TRUTER, M. R. (1961). *Acta Cryst.* **14**, 318.  
 TRUTER, M. R., CRUICKSHANK, D. W. J. & JEFFREY, G. A. (1960). *Acta Cryst.* **13**, 855.  
 VAN UITERT, L. G. & SODEN, R. R. (1961). *Advances in the Chemistry of Coordination Compounds*, p. 613. New York: MacMillan & Co.  
 VIJAYAN, M. & VISWAMITRA, M. A. (1965). *Indian J. Pure App. Physics*, **3**, 357.  
 WELLS, A. F. (1962). *Structural Inorganic Chemistry*. Oxford: Clarendon Press.  
 ZACHARIASEN, W. H. & PLETINGER, H. A. (1959). *Acta Cryst.* **12**, 526.

*Acta Cryst.* (1966). **21**, 532

## The Crystal and Molecular Structure of 4-(1,5-Diazabicyclo[3.2.1]oct-8-yl)pyridine, $C_{11}H_{15}N_3$

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4-(1,5-Diazabicyclo[3.2.1]oct-8-yl)pyridine crystallizes in the orthorhombic space group  $Pnma$  with four molecules in the unit cell. The lattice parameters are  $a = 13.58$ ,  $b = 10.99$ ,  $c = 6.93$  Å.

The structure was obtained by determining the phases directly from the structure factor magnitudes by means of the symbolic addition procedure. The structure was refined by means of three-dimensional least-squares to a final  $R = 12.4\%$  for the observed data.

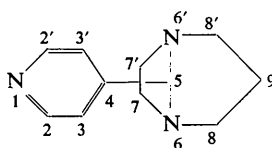
The molecule has a plane of symmetry. The cage portion consists of puckered five-, six- and seven-membered rings. The six-membered ring is in the chair configuration whereas the seven-membered ring has the boat configuration. The bond lengths in the pyridine ring resemble those in a quinoid type structure.

### Introduction

One portion of 4-(1,5-diazabicyclo[3.2.1]oct-8-yl)pyridine consists of a cage formed by a five-, six- and seven-membered ring. The investigation of the struc-

ture was undertaken to determine the stereoconfiguration of the cage, since several different models of the molecule appear *a priori* to be equally probable. The molecule lies on a plane of symmetry and for the pres-

ent purpose the atoms are numbered in the following manner:



### Experimental

The material was obtained from the Aldrich Chemical Company. It crystallizes in the form of yellowish transparent rectangular prisms. The crystal used was elongated in the *c* direction and had a cross-section of  $0.3 \times 0.3$  mm. With the crystal mounted parallel to the *c* axis, multiple-film, equi-inclination Weissenberg photographs were taken with Cu  $K\alpha$  radiation and a nickel filter. Data were collected from the zero through the fifth layer. A total of 817 independent reflections were recorded of which 655 were observed to have intensities greater than zero. The intensities were estimated visually by comparison with a calibrated film strip.

Cell parameters were determined from precession photographs with the crystal mounted parallel to the *c* axis. They are

$$\begin{aligned} a &= 13.58 \pm 0.03 \text{ \AA} \\ b &= 10.99 \pm 0.03 \\ c &= 6.93 \pm 0.02 \\ \alpha &= \beta = \gamma = 90^\circ, \end{aligned}$$

and  $Z=4$  corresponding to a  $\rho_{x\text{-ray}} = 1.213 \text{ g.cm}^{-3}$ . From the systematic absences, the space group could be either  $Pna2_1$  or  $Pnma$ . The statistical averages of the intensity data indicated that the crystal was centrosymmetric, hence the space group  $Pnma$  was chosen. This space group requires eight equivalent positions whereas there are only four molecules in the unit cell. Since the molecule is acentric, it must possess a plane of symmetry and this plane must be placed at  $y = \frac{1}{4}$ .

The intensities were corrected for Lorentz and polarization factors and spot size. No absorption correction was applied. The data were placed on an absolute scale by means of a *K*-curve (Karle & Hauptman, 1953) and both structure factor magnitudes,  $|F|$ , and normalized structure factor magnitudes,  $|E|$ , were computed. For space group  $Pnma$ ,

$$E_{\mathbf{h}}^2 = F_{\mathbf{h}}^2 / \varepsilon \sum_{j=1}^N f_{j\mathbf{h}}^2 \quad (1)$$

where  $\varepsilon=2$  when  $\mathbf{h}$  is  $hk0$  or  $0kl$ , otherwise  $\varepsilon=1$ ,  $N$  is the total number of atoms in the unit cell,  $f_{j\mathbf{h}}$  is the atomic scattering factor for the  $j$ th atom and the  $F_{\mathbf{h}}^2$  are placed on an absolute scale and corrected for thermal motion.

The statistical averages and distributions for the normalized structure factors are compared in Table 1 with theoretical values calculated by assuming random

distribution of atoms in the unit cell. The experimental values are consistent with a centrosymmetric crystal.

Table 1. Statistical averages and distributions of  $|E|$

	Experimental	Centro-symmetric	Noncentro-symmetric
$\langle  E  \rangle$	0.755	0.798	0.886
$\langle  E ^2 - 1 \rangle$	0.988	0.968	0.736
$\langle  E ^2 \rangle$	0.997	1.000	1.000
$ E  > 3$	0.7%	0.3%	0.01%
$ E  > 2$	4.3	5.0	1.8
$ E  > 1$	24.0	32.0	36.8

### Structure determination

The structure was solved by obtaining the values of the phases directly from the structure factor magnitudes by means of the symbolic addition procedure (see e.g. Karle & Karle, 1963, 1964, 1965; Karle, Britts & Gum, 1964; Karle & Britts, 1966). The phase determination for this crystal was rather routine and merits no special discussion. The three origin specifying signs (reflections 12,5,0, 291, and 743 all assigned +) plus one unknown sign for reflection 890 designated as  $x$  were used to obtain one hundred additional signs for reflections with  $|E| > 1.4$ . The probability of a sign indication was never permitted to be less than 0.97. The value of  $x$  remained unknown; therefore two  $E$  maps (Karle, Hauptman, Karle & Wing, 1958) were computed. The one with  $x \equiv +$  was obviously in error while the other one with  $x \equiv -$  revealed unequivocally the coordinates of the seven carbon atoms and two nitrogen atoms in the asymmetric unit.

The coordinates, as obtained from the  $E$  map, were subjected to a least-squares refinement using a modification of the ORFLS program (Busing, Martin & Levy, 1962). The function which was minimized was  $\Sigma(F_o - F_c)^2$ . Individual scale factors were refined during the isotropic refinement and then kept constant for the anisotropic refinement. Since the molecule has a plane of symmetry, the four atoms N(1), C(4), C(5), and C(9) which lie on the plane of symmetry ( $y = \frac{1}{4}$ ) need special treatment to describe their vibrations. Accordingly,  $\beta_{12}$  and  $\beta_{23}$  were set equal to zero in the terms of the anisotropic temperature factors for these four atoms. Toward the end of the refinement a difference map (Fig. 1) was computed to locate the hydrogen atoms. All seven independent hydrogen atoms on the aliphatic portion of the molecule were located, but the two independent hydrogen atoms on the pyridine ring were not found. Further least-squares refinement on the heavy atoms with the coordinates of seven hydrogen atoms kept constant resulted in an  $R$  value of 12.4% for the observed data. Table 2 lists the observed and calculated structure factors.

The parameters for the heavy atoms are given in Table 3 and the hydrogen coordinates as read from the difference map are shown in Table 4. Sections from a three-dimensional density map computed with these parameters are shown in Fig. 1.

Table 2. Observed and calculated structure factors

H	K	L	Y(OBS)	Y(CALC)
0	0	0	23.9	-24.1
0	0	1	1.2	-1.2
0	0	2	3.2	-3.2
0	0	3	7.9	-7.9
0	0	4	10.8	-10.8
0	0	5	7.9	-7.9
0	0	6	10.8	-10.8
0	0	7	7.9	-7.9
0	0	8	10.8	-10.8
0	0	9	7.9	-7.9
0	0	10	10.8	-10.8
0	0	11	7.9	-7.9
0	0	12	10.8	-10.8
0	0	13	7.9	-7.9
0	0	14	10.8	-10.8
0	0	15	7.9	-7.9
0	0	16	10.8	-10.8
0	0	17	7.9	-7.9
0	0	18	10.8	-10.8
0	0	19	7.9	-7.9
0	0	20	10.8	-10.8
0	0	21	7.9	-7.9
0	0	22	10.8	-10.8
0	0	23	7.9	-7.9
0	0	24	10.8	-10.8
0	0	25	7.9	-7.9
0	0	26	10.8	-10.8
0	0	27	7.9	-7.9
0	0	28	10.8	-10.8
0	0	29	7.9	-7.9
0	0	30	10.8	-10.8
0	0	31	7.9	-7.9
0	0	32	10.8	-10.8
0	0	33	7.9	-7.9
0	0	34	10.8	-10.8
0	0	35	7.9	-7.9
0	0	36	10.8	-10.8
0	0	37	7.9	-7.9
0	0	38	10.8	-10.8
0	0	39	7.9	-7.9
0	0	40	10.8	-10.8
0	0	41	7.9	-7.9
0	0	42	10.8	-10.8
0	0	43	7.9	-7.9
0	0	44	10.8	-10.8
0	0	45	7.9	-7.9
0	0	46	10.8	-10.8
0	0	47	7.9	-7.9
0	0	48	10.8	-10.8
0	0	49	7.9	-7.9
0	0	50	10.8	-10.8
0	0	51	7.9	-7.9
0	0	52	10.8	-10.8
0	0	53	7.9	-7.9
0	0	54	10.8	-10.8
0	0	55	7.9	-7.9
0	0	56	10.8	-10.8
0	0	57	7.9	-7.9
0	0	58	10.8	-10.8
0	0	59	7.9	-7.9
0	0	60	10.8	-10.8
0	0	61	7.9	-7.9
0	0	62	10.8	-10.8
0	0	63	7.9	-7.9
0	0	64	10.8	-10.8
0	0	65	7.9	-7.9
0	0	66	10.8	-10.8
0	0	67	7.9	-7.9
0	0	68	10.8	-10.8
0	0	69	7.9	-7.9
0	0	70	10.8	-10.8
0	0	71	7.9	-7.9
0	0	72	10.8	-10.8
0	0	73	7.9	-7.9
0	0	74	10.8	-10.8
0	0	75	7.9	-7.9
0	0	76	10.8	-10.8
0	0	77	7.9	-7.9
0	0	78	10.8	-10.8
0	0	79	7.9	-7.9
0	0	80	10.8	-10.8
0	0	81	7.9	-7.9
0	0	82	10.8	-10.8
0	0	83	7.9	-7.9
0	0	84	10.8	-10.8
0	0	85	7.9	-7.9
0	0	86	10.8	-10.8
0	0	87	7.9	-7.9
0	0	88	10.8	-10.8
0	0	89	7.9	-7.9
0	0	90	10.8	-10.8
0	0	91	7.9	-7.9
0	0	92	10.8	-10.8
0	0	93	7.9	-7.9
0	0	94	10.8	-10.8
0	0	95	7.9	-7.9
0	0	96	10.8	-10.8
0	0	97	7.9	-7.9
0	0	98	10.8	-10.8
0	0	99	7.9	-7.9
0	0	100	10.8	-10.8
0	0	101	7.9	-7.9
0	0	102	10.8	-10.8
0	0	103	7.9	-7.9
0	0	104	10.8	-10.8
0	0	105	7.9	-7.9
0	0	106	10.8	-10.8
0	0	107	7.9	-7.9
0	0	108	10.8	-10.8
0	0	109	7.9	-7.9
0	0	110	10.8	-10.8
0	0	111	7.9	-7.9
0	0	112	10.8	-10.8
0	0	113	7.9	-7.9
0	0	114	10.8	-10.8
0	0	115	7.9	-7.9
0	0	116	10.8	-10.8
0	0	117	7.9	-7.9
0	0	118	10.8	-10.8
0	0	119	7.9	-7.9
0	0	120	10.8	-10.8
0	0	121	7.9	-7.9
0	0	122	10.8	-10.8
0	0	123	7.9	-7.9
0	0	124	10.8	-10.8
0	0	125	7.9	-7.9
0	0	126	10.8	-10.8
0	0	127	7.9	-7.9
0	0	128	10.8	-10.8
0	0	129	7.9	-7.9
0	0	130	10.8	-10.8
0	0	131	7.9	-7.9
0	0	132	10.8	-10.8
0	0	133	7.9	-7.9
0	0	134	10.8	-10.8
0	0	135	7.9	-7.9
0	0	136	10.8	-10.8
0	0	137	7.9	-7.9
0	0	138	10.8	-10.8
0	0	139	7.9	-7.9
0	0	140	10.8	-10.8
0	0	141	7.9	-7.9
0	0	142	10.8	-10.8
0	0	143	7.9	-7.9
0	0	144	10.8	-10.8
0	0	145	7.9	-7.9
0	0	146	10.8	-10.8
0	0	147	7.9	-7.9
0	0	148	10.8	-10.8
0	0	149	7.9	-7.9
0	0	150	10.8	-10.8
0	0	151	7.9	-7.9
0	0	152	10.8	-10.8
0	0	153	7.9	-7.9
0	0	154	10.8	-10.8
0	0	155	7.9	-7.9
0	0	156	10.8	-10.8
0	0	157	7.9	-7.9
0	0	158	10.8	-10.8
0	0	159	7.9	-7.9
0	0	160	10.8	-10.8
0	0	161	7.9	-7.9
0	0	162	10.8	-10.8
0	0	163	7.9	-7.9
0	0	164	10.8	-10.8
0	0	165	7.9	-7.9
0	0	166	10.8	-10.8
0	0	167	7.9	-7.9
0	0	168	10.8	-10.8
0	0	169	7.9	-7.9
0	0	170	10.8	-10.8
0	0	171	7.9	-7.9
0	0	172	10.8	-10.8
0	0	173	7.9	-7.9
0	0	174	10.8	-10.8
0	0	175	7.9	-7.9
0	0	176	10.8	-10.8
0	0	177	7.9	-7.9
0	0	178	10.8	-10.8
0	0	179	7.9	-7.9
0	0	180	10.8	-10.8
0	0	181	7.9	-7.9
0	0	182	10.8	-10.8
0	0	183	7.9	-7.9
0	0	184	10.8	-10.8
0	0	185	7.9	-7.9
0	0	186	10.8	-10.8
0	0	187	7.9	-7.9
0	0	188	10.8	-10.8
0	0	189	7.9	-7.9
0	0	190	10.8	-10.8
0	0	191	7.9	-7.9
0	0	192	10.8	-10.8
0	0	193	7.9	-7.9
0	0	194	10.8	-10.8
0	0	195	7.9	-7.9
0	0	196	10.8	-10.8
0	0	197	7.9	-7.9
0	0	198	10.8	-10.8
0	0	199	7.9	-7.9
0	0	200	10.8	-10.8

Table 3. Fractional coordinates for 4-(1,5-diazabicyclo[3.2.1]oct-8-yl)pyridine

The thermal parameters are of the form  $T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .  
Each thermal parameter is multiplied by  $10^4$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
N(1)	0.1482	0.2500	0.3209	39	76	115	0	31	0
C(2)	0.1927	0.1459	0.2583	48	58	132	-4	15	12
C(3)	0.2730	0.1414	0.1458	42	33	165	1	15	33
C(4)	0.3184	0.2500	0.0829	25	33	94	0	8	0
C(5)	0.4088	0.2500	0.9646	32	43	22	0	-7	0
N(6)	0.4115	0.1427	0.8323	32	46	67	9	-7	-33
C(7)	0.3433	0.1769	0.6819	43	70	152	-6	-27	-14
C(8)	0.5135	0.1341	0.7596	42	116	128	22	+22	-33
C(9)	0.5468	0.2500	0.6474	37	227	77	0	+35	0
Standard deviations									
N	0.0004	0.0004	0.0013	3	6	27	3	8	8
C	0.0005	0.0006	0.0016	3	6	35	4	9	12

### The structure

The configuration of the molecule is shown in the stereo diagrams in Fig. 2. These diagrams were drawn by a computer with the ORTEP program (Johnson,

1965). The pyridine ring is planar. The equation of the least-squares plane is

$$7.9085x + 5.6537z = 2.9846, \quad (2)$$

where the value on the right-hand side of the equation is equal to the origin-to-plane distance in Å (Schomaker, Waser, Marsh & Bergman, 1959). The maximum deviation of any atom in the pyridine ring from this plane is 0.0021 Å. Atom C(5), which is attached to the ring, is +0.048 Å out of the plane of the ring.

In the cage portion of the molecule, atoms C(5), N(6), C(8), C(9), C(8') and N(6') form a somewhat distorted, six-membered ring in the chair configuration. The seven-membered ring formed by C(7), N(6), C(8), C(9), C(8'), N(6') and C(7') is in a boat configuration. In the five-membered ring, atom C(5) is 0.64 Å out of the plane formed by atoms N(6), C(7), C(7') and N(6').

The bond distances and angles are shown in Fig. 3. The one unusual distance in the cage is C(7)–C(7')

Table 4. Approximate coordinates for the hydrogen atoms

Atom	<i>x</i>	<i>y</i>	<i>z</i>
H(5)	0.463	0.250	0.058
H(7)	0.280	0.145	0.712
H(71)	0.367	0.163	0.522
H(8)	0.517	0.058	0.650
H(81)	0.562	0.107	0.900
H(9)	0.522	0.250	0.492
H(91)	0.622	0.250	0.647

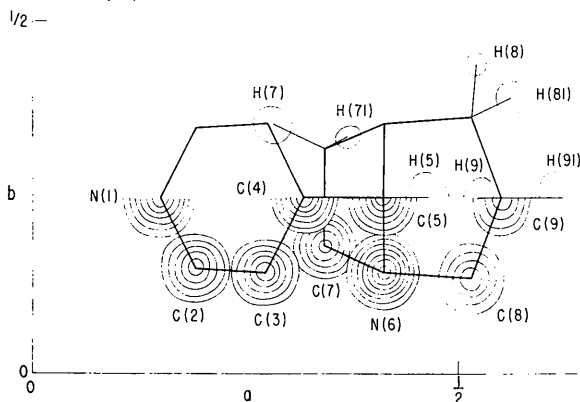


Fig. 1. The lower portion shows the final composite electron density map projected onto (001). The contours are equally spaced at  $1 \text{ e.}\text{\AA}^{-3}$  and begin at  $1 \text{ e.}\text{\AA}^{-3}$ . The upper portion shows a difference map which revealed seven of the nine hydrogen atoms. The contours are at  $0.5 \text{ e.}\text{\AA}^{-3}$ .

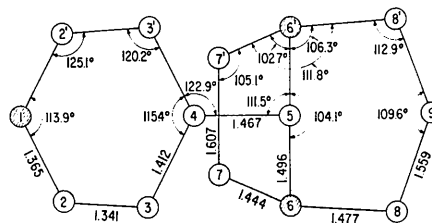


Fig. 3. Bond distances and angles. The standard deviations for the bond distances range from 0.009 to 0.013 Å and the standard deviations for the angles are about  $1.0^\circ$ . To account for possible systematic experimental errors, it is reasonable to increase the standard deviations by a factor of two.

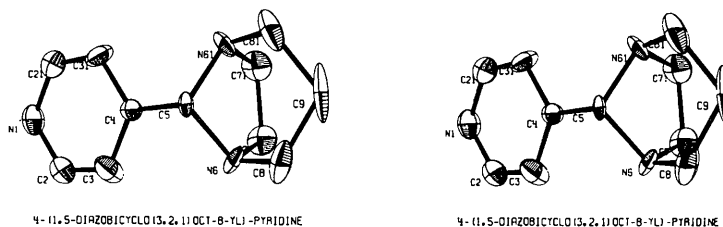


Fig. 2. Stereoconfiguration of 4-(1,5-diazabicyclo[3.2.1]oct-8-yl)-pyridine.

1.61 Å. Even allowing for a fairly large error in the bond length, the value is still larger than is usually observed for single C–C bonds. The strains introduced by the bonding to form the cage, especially in closing the C(7)–C(7') bond, are probably relieved by this somewhat long bond.

The distances and angles in the pyridine ring are also somewhat unusual. The bond formed by C(2)–C(3) is only 1.34 Å as compared with 1.41 Å for C(3)–C(4). Also, C(4)–C(5) at 1.47 Å is considerably shorter than a single-bond value. The arrangements of the bond lengths resemble those from a quinoid type structure:

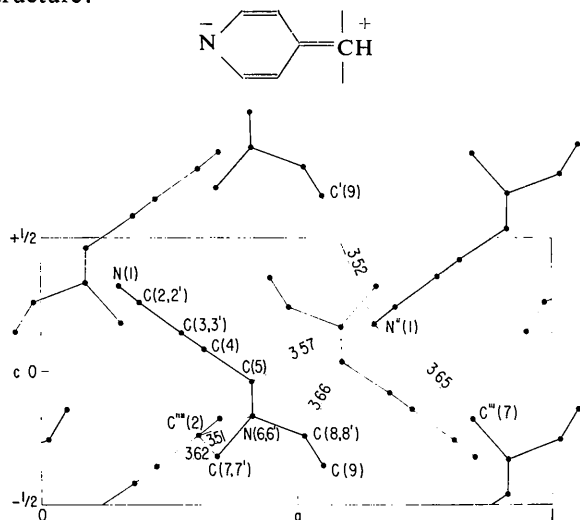


Fig. 4. The contents of a unit cell viewed along the *b* axis. All the intermolecular distances less than 3.8 Å are indicated in the figure.

A similar situation has been found for 4-nitropyridine *N*-oxide (Eichhorn, 1956) with bond lengths and angles in the pyridine ring almost identical with those found in the present investigation.

Fig. 4 illustrates the contents of the unit cell and the nearest approaches between molecules. N(1) of the pyridine ring is surrounded by six atoms of neighboring molecules at distances of 3.52–3.66 Å. The only other near approach is in the *b* direction between atoms C(2) of one molecule and N(6) and C(7) of another at 3.51 and 3.62 Å.

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#### References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). ORFLS, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.
- EICHHORN, E. L. (1956). *Acta Cryst.* **9**, 787.
- JOHNSON, C. K. (1965). ORTEP, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.
- KARLE, I. L. & BRITTS, K. (1966). *Acta Cryst.* **20**, 118.
- KARLE, I. L., BRITTS, K. & GUM, P. (1964). *Acta Cryst.* **17**, 496.
- KARLE, J. & HAUPTMAN, H. (1953). *Acta Cryst.* **6**, 473.
- KARLE, I. L., HAUPTMAN, H., KARLE, J. & WING, A. B. (1958). *Acta Cryst.* **11**, 257.
- KARLE, I. L. & KARLE, J. (1963). *Acta Cryst.* **16**, 969.
- KARLE, I. L. & KARLE, J. (1964). *Acta Cryst.* **17**, 1356.
- KARLE, I. L. & KARLE, J. (1965). *Acta Cryst.* **18**, 345.
- SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* **12**, 600.

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## The Crystal Structure of Zinc Dimethyldithiocarbamate

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The crystal structure of zinc dimethyldithiocarbamate, Zn[S<sub>2</sub>CN(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, has been determined from three-dimensional Weissenberg data and refined by anisotropic least-squares methods. The crystals are monoclinic, space group *C2/c*, with *a* = 8.455 ± 0.003, *b* = 15.747 ± 0.005, *c* = 18.345 ± 0.009 Å, β = 104.76 ± 0.04°. The cell contains the content of eight monomeric molecules.

The most interesting finding is the binuclear nature of molecules of the compound in the crystal. These binuclear molecules, of formula Zn<sub>2</sub>[S<sub>2</sub>CN(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>, lie on twofold axes. The coordination of sulfur about each zinc atom is distorted tetrahedral, with the average Zn–S distance 2.362 Å. The Zn···Zn distance in the molecule is 3.973 Å. The dimethyldithiocarbamate groups deviate slightly from planarity, and are of two types. Each group of the first type is chelated directly to its own zinc atom of a tetrahedron, then two of the second type act as bridging ligands between the two zinc–sulfur tetrahedra in the molecule. The molecule appears not to vibrate or librate as a rigid body. Intermolecular distances are completely normal.

#### Introduction

The dithiocarbamates find wide application in inorganic analysis, in rubber chemistry and technology, and

in agriculture as fungicides. Nevertheless, despite our increasing knowledge of dithiocarbamate chemistry, their mode of action as biocides has not yet been