Acta Cryst. (1965). **19**, 614

The Crystal and Molecular Structure of the Hydrobromide of 3-Methoxycarbonyl-*trans*-3,5-dimethyl-Δ¹-pyrazoline

By Hartwig Luth and James Trotter

Department of Chemistry, University of British Columbia, Vancouver 8, *B. C., Canada*

(*Received* 18 *February* 1965)

Crystals of the hydrobromide of 3-methoxycarbonyl-*trans*-3,5-dimethyl-Δ^1-pyrazoline, $C_7H_{13}N_2O_2Br$, are monoclinic, $a=8{\cdot}28$, $b=10{\cdot}31$, $c=13{\cdot}92$ Å, $\beta=122{\cdot}4°$, $Z=4$, space group $P2_1/c$. The structure was determined by three-dimensional heavy-atom Patterson and Fourier methods, using visually estimated Cu $K\alpha$ data. Positional and anisotropic thermal parameters were refined by least-squares, the final R value being 0·116 for 409 observed reflexions.

The analysis indicates that the compound is not a simple hydrobromide of the Δ^1-pyrazoline, but contains a cation with no double-bond in the ring, with a trigonal C(5) atom, and with the positive charge distributed between N(1) and C(5). The five membered-ring is non-planar, and can be described in terms either of N(2) displaced by 0·32 Å from the plane of the other four atoms, or of N(1) and N(2) displaced on opposite sides of the plane of the three carbon atoms. The methyl group on C(5) lies almost on these planes. Apart from these unusual features the other molecular dimensions are normal. The shortest intermolecular contact is a C(5) · · · O(3) distance of 2·76 Å, this short approach being a result of attraction between the positively charged carbon and the relatively negative oxygen. The shortest contact involving the bromide ion is a $Br^- \cdots H\text{–}N(2)$ hydrogen bond of 3·22 Å, the next shortest being $Br^- \cdots N(2)=3{\cdot}31$ Å. The other distances are normal.

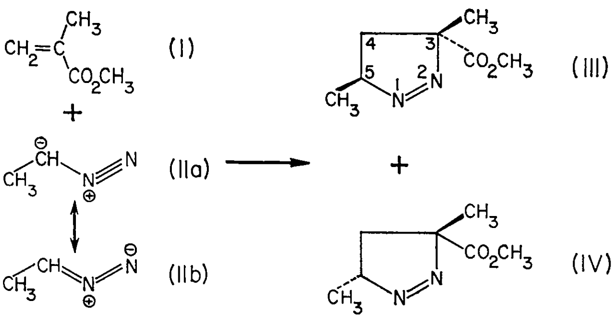
Introduction

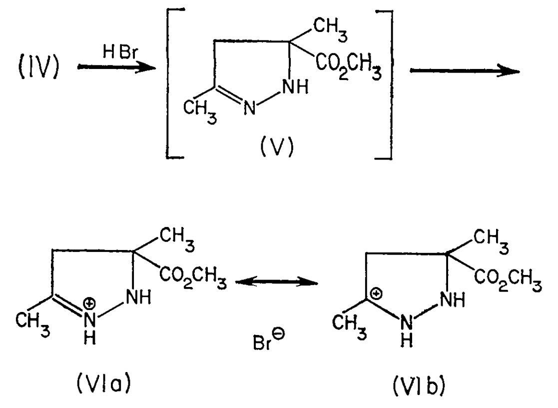
Reaction of methyl methacrylate (I) with diazoethane (II) produces two isomeric 3,5-dimethyl-3-methoxycarbonyl-Δ^1-pyrazolines, (III) and (IV), which can be separated by distillation with a spinning-band column (McGreer, Morris & Carmichael, 1963; McGreer, Chiu, Vinje & Wong, 1965). The lower-boiling isomer has been assigned the *cis* structure (III) and the higher-boiling isomer the *trans* structure (IV), on the basis of nuclear magnetic resonance spectra, and of the products of photolysis. To establish the structures conclusively, and to investigate the geometry of the ring system, an X-ray analysis has now been carried out of the hydrobromide of the higher-boiling isomer (tentatively 3-methoxycarbonyl-*trans*-3,5-dimethyl-Δ^1-pyrazoline, IV).

The results of the X-ray analysis, which are described in the present paper, indicate that the cation of the hydrobromide can best be represented as a resonance hybrid of (VI*a*) and (VI*b*), that is with the positive charge distributed between N(1) and C(5). Formation of this structure involves initially rearrangement to a Δ^2-pyrazoline (V), followed by formation of the hydrobromide. Unfortunately the results do not solve the original problem, as C(5) is a trigonal atom in the hydrobromide, so that there is no question of *cis–trans* isomerism. However the unusual structure of the hydrobromide is probably of more interest than that of the original pyrazoline.

Experimental

Crystals of the hydrobromide of 3-methoxycarbonyl-*trans*-3,5-dimethyl-Δ^1-pyrazoline are colourless plates with (100) developed and smaller {011} faces. The density was measured by flotation in a carbon tetrachloride–benzene mixture, and the unit-cell dimensions and space group were determined from various rotation, Weissenberg and precession films.





Crystal data (λ Cu $K\alpha = 1{\cdot}5418$ Å; λ Mo $K\alpha = 0{\cdot}7107$ Å)
3-Methoxycarbonyl-*trans*-3,5-dimethyl-Δ^1-pyrazoline hydrobromide, $C_7H_{13}N_2O_2Br$; M.W.237·1; m.p. 152 – 153 °C.
Monoclinic, $a = 8{\cdot}28 \pm 0{\cdot}03$, $b = 10{\cdot}31 \pm 0{\cdot}03$, $c = 13{\cdot}92 \pm 0{\cdot}03$ Å, $\beta = 122{\cdot}4° \pm 0{\cdot}3°$.
$U = 1003$ Å^3.
$D_m = 1{\cdot}56$ g.cm^{-3}, $Z = 4$, $D_x = 1{\cdot}57$ g.cm^{-3}.
Absorption coefficient for Cu $K\alpha$ X-rays $\mu = 59$ cm^{-1}.
$F(000) = 480$.
Absent reflexions: $h0l$ when l is odd, $0k0$ when k is odd.
Space group $P2_1/c$ (C_{2h}^5).

The intensities of the reflexions were recorded on equi-inclination Weissenberg films of the $h0l$, $h1l \cdots h5l$ zones, for a crystal rotating about the b axis, using Cu $K\alpha$ radiation. The intensities were estimated visually, Lorentz and polarization factors were applied, and the structure amplitudes were derived. The crystal used was a plate with edge 0·3 mm parallel to [011], and thickness 0·1 mm, so that absorption errors are not too severe, and no corrections were applied. The various layers were scaled initially by carefully timing the exposures, and the scale factors were adjusted slightly at one stage in the analysis by comparison with the calculated structure factors. The photographs showed a rapid fall-off in intensity with increasing Bragg angle, and only 409 reflexions had measurable intensities.

Structure analysis

The position of the bromide ion was determined from the three-dimensional Patterson function as (0·121, 0·202, 0·018), structure factors were calculated ($R = 0{\cdot}39$ for the 409 observed reflexions), and a three-dimensional Fourier series was summed, with signs of the structure amplitudes derived from the bromide ion contributions. On the resulting electron-density map all the atoms in the molecule (except hydrogen) were resolved. Structure factors were calculated, with the scattering factors for Br$^-$, C, N, O of *International Tables for X-ray Crystallography* (1962); that for Br$^-$ was derived from the Br curve and was corrected for anomalous dispersion, and the temperature factor, B, was taken as 5·0 Å^2 for all the atoms. R was 0·28.

The positional and thermal parameters, and an overall scale factor, were refined by block-diagonal least-squares, minimizing $\Sigma w(F_o - F_c)^2$, with $\sqrt{w} = |F_o|/60$ when $|F_o| < 60$, and $\sqrt{w} = 60/|F_o|$ when $|F_o| \geq 60$. After three cycles of refinement using isotropic temperature factors, the scale factors of the individual layers were adjusted slightly by equating the sums of $|F_o|$ and $|F_c|$ for each layer. At this stage the B value for N(1) was anomalously high, so that it seemed likely that this atom carried the positive charge, and the N$^+$ scattering factor (derived from the N curve) was used for this atom in subsequent cycles. Four more least-squares cycles, with anisotropic thermal parameters, reduced R to 0·116 for the 409 observed reflexions, and completed the refinement. Measured and calculated structure factors are listed in Table 1.

A final three-dimensional Fourier series was summed, and superimposed sections of the resulting electron-density distribution taken through the atomic centres are shown in Fig. 1.

Coordinates and molecular dimensions

The final positional and thermal parameters are given in Table 2; x, y and z are fractional parameters, $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ their standard deviations (Å) computed from the least-squares residuals, B the isotropic thermal parameters (from the third least-squares cycle),

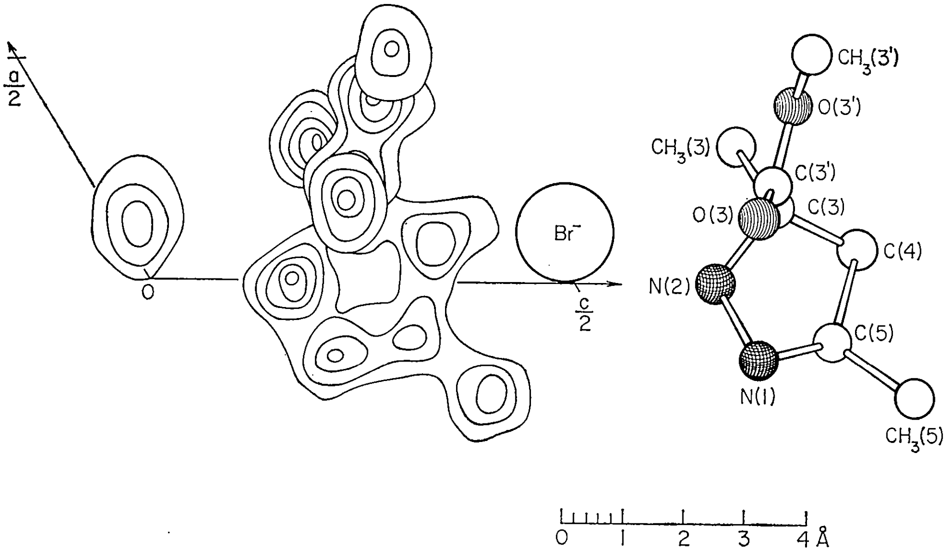


Fig. 1. Superimposed sections of the three-dimensional electron-density distribution, through the atomic centres parallel to (010); contours at intervals of 1, 2, 3... e.Å^{-3} for the light atoms, and 10, 20, 30 e.Å^{-3} for bromine. A perspective drawing of the molecule is also shown.

and b_{ij} the anisotropic thermal parameters in the expression:

$$\exp\{-(b_{11}h^2+b_{12}hk+b_{13}hl+b_{22}k^2+b_{23}kl+b_{33}l^2)\}.$$

The b_{ij} are greatly affected by inaccuracies in measured structure factors, such as absorption errors, and in addition the values are not completely independent of one another, since the rescaling of the layers tends to make b_{22} on the average equal to the mean of b_{11} and b_{33}. No particular significance can therefore be attached to detailed variations, and the thermal parameters will not be discussed further.

The bond distances and valency angles in the molecule are shown in Fig. 2; the standard deviations average about 0·06 Å for bonds and 3° for angles. Various planes through the five-membered ring were computed, and these indicated that the ring is not completely planar. Two different descriptions give equally satisfactory accounts of the ring geometry. The first is in terms of the plane through the four atoms N(1), C(3), C(4), C(5), which has equation:

$$0{\cdot}0127X'+0{\cdot}9525Y+0{\cdot}3043Z'=1{\cdot}1693, \qquad (1)$$

Table 1. *Measured and calculated structure factors*

h	k	l	F_{obs}	F_{calc}
0	0	2	10.6	6.2
0	0	4	87.9	92.4
0	0	6	63.8	68.0
0	0	8	17.6	15.9
0	0	10	28.4	23.7
0	0	12	0.	0.0
1	0	0	122.2	130.1
1	0	-2	28.3	-22.5
1	0	2	38.8	49.5
1	0	-4	161.3	159.4
1	0	4	0.	1.9
1	0	-6	104.8	102.2
1	0	6	35.8	40.4
1	0	-8	74.9	76.8
1	0	8	0.	-9.7
1	0	-10	27.3	26.3
1	0	10	0.	-8.7
1	0	-12	28.7	31.6
1	0	12	0.	-8.6
2	0	0	14.0	-10.8
2	0	-2	81.8	75.6
2	0	2	48.8	43.6
2	0	-4	32.6	34.3
2	0	4	67.2	-64.9
2	0	-6	40.3	40.3
2	0	6	25.5	-28.1
2	0	-8	58.5	59.3
2	0	-10	29.4	29.4
2	0	-12	49.9	53.9
3	0	0	80.3	-84.3
3	0	-2	51.4	-48.6
3	0	2	21.0	-41.5
3	0	-4	66.3	-65.4
3	0	4	39.1	-40.8
3	0	-6	62.2	61.0
3	0	6	34.3	-34.5
3	0	-8	0.	-2.9
3	0	-10	18.3	23.6
3	0	-12	28.6	26.3
4	0	0	43.8	-42.9
4	0	-2	44.6	-50.9
4	0	2	49.6	-49.7
4	0	-4	93.3	-91.4
4	0	4	27.8	-27.2
4	0	-6	0.	-19.5
4	0	6	0.	-14.4
4	0	-8	82.8	-83.4
4	0	8	0.	-12.6
4	0	10	0.	-2.7
5	0	0	25.7	-32.1
5	0	-2	47.5	-51.3
5	0	2	19.8	-16.1
5	0	-4	64.5	-66.6
5	0	-6	28.3	-32.4
5	0	-8	60.4	-59.3
5	0	-10	46.6	-45.9
5	0	-12	24.8	-24.6
5	0	-14	19.7	-27.0
6	0	-4	0.	-8.2
6	0	-6	26.0	-37.0
6	0	-8	42.3	-47.2
6	0	-10	44.3	-44.7
6	0	-12	28.8	-27.3
6	0	-14	19.4	-25.0
7	0	-14	18.5	-28.5
0	1	1	18.2	12.9
0	1	3	80.9	66.5
0	1	5	0.	1.7
0	1	7	36.6	42.0
0	1	9	0.	-18.3
0	1	11	0.	9.4
1	1	-1	54.5	53.3
1	1	1	22.5	24.3
1	1	-3	23.3	18.0
1	1	3	0.	2.2
1	1	5	0.	-0.5
1	1	-5	40.1	34.6
1	1	-7	22.1	22.4
1	1	7	0.	8.5
1	1	-9	0.	1.3
1	1	9	0.	-9.8
1	1	-11	24.7	25.6
2	1	-1	0.	-1.4
2	1	1	16.5	12.5
2	1	-3	14.2	-16.3
2	1	3	33.4	-33.3
2	1	-5	62.9	59.1
2	1	5	14.4	18.3
2	1	-7	0.	-0.7
2	1	7	0.	-16.6
2	1	-9	14.9	15.2
3	1	-1	0.	-12.8
3	1	1	11.9	-9.4
3	1	-3	15.7	11.3
3	1	3	39.6	-37.1
3	1	-5	34.0	-25.7
3	1	-7	0.	-6.8
3	1	-9	14.7	13.8
3	1	-11	0.	2.8
4	1	-1	0.	-16.6
4	1	1	0.	-8.2
4	1	-3	26.8	-24.5
4	1	-5	38.5	-37.3
4	1	-7	0.	2.2
4	1	-9	0.	0.3
4	1	-11	20.6	-21.9
4	1	-13	0.	9.8
4	1	-15	0.	-4.3
5	1	1	0.	-1.1
5	1	-1	0.	1.3
5	1	-3	28.4	-30.9
5	1	-5	0.	-8.2
5	1	-7	14.6	-15.3
5	1	-9	19.3	-21.8
5	1	-11	17.1	-15.4
6	1	1	0.	7.3
6	1	-1	0.	5.5
6	1	-3	28.3	-24.3
6	1	-5	0.	1.1
6	1	-7	0.	1.1
6	1	-9	20.5	-27.4
6	1	-11	0.	0.1
0	2	2	152.5	-140.0
0	2	4	87.2	-84.9
0	2	6	0.	-12.2
0	2	8	30.9	-29.2
1	2	0	9.4	1.1
1	2	-2	88.7	-88.0
1	2	2	34.4	-42.1
1	2	-4	125.5	-109.2
1	2	4	32.1	-34.4
1	2	-6	32.8	-34.4
1	2	6	12.7	-7.6
1	2	-8	73.0	-67.1
1	2	8	0.	4.0
1	2	-10	37.0	-36.5
1	2	10	19.2	3.2
1	2	-12	0.	-13.9
1	2	12	0.	5.8
2	2	0	7.9	-11.6
2	2	-2	57.4	-55.2
2	2	2	13.7	15.2
2	2	-4	46.3	-43.4
2	2	4	0.	9.8
2	2	-6	10.1	-7.8
2	2	6	0.	18.5
2	2	-8	55.3	-51.5
2	2	8	22.2	25.7
2	2	-10	38.6	-34.8
2	2	-12	19.3	-24.9
2	2	-14	17.2	-18.3
3	2	0	53.3	56.2
3	2	-2	9.1	20.3
3	2	2	44.0	46.0
3	2	-4	29.4	24.8
3	2	4	19.5	30.9
3	2	-6	10.5	6.3
3	2	-8	27.6	-29.7
3	2	-10	14.4	-14.0
3	2	-12	11.1	-16.6
3	2	-14	14.8	-14.0
4	2	0	38.7	41.8
4	2	-2	31.6	42.1
4	2	2	23.9	27.8
4	2	-4	39.3	40.1
4	2	4	21.7	23.2
4	2	-6	65.1	62.9
4	2	-8	22.2	27.2
4	2	-10	0.	7.1
4	2	-12	15.7	16.7
4	2	-14	0.	-11.1
5	2	0	20.2	25.4
5	2	-2	37.5	36.3
5	2	-4	22.1	33.1
5	2	-6	54.8	55.9
5	2	-8	27.5	31.7
5	2	-10	21.1	17.9
5	2	-12	41.6	44.9
6	2	0	0.	4.2
6	2	2	0.	-3.0
6	2	-2	0.	3.1
6	2	-4	20.6	24.7
6	2	-6	27.0	27.5
6	2	-8	18.2	25.4
6	2	-10	34.5	31.0
6	2	-12	35.2	35.2
0	3	1	69.2	-74.1
0	3	3	77.3	-76.7
0	3	5	58.4	-57.2
0	3	7	16.3	-21.0
1	3	-1	99.0	-97.6
1	3	1	22.5	-34.9
1	3	-3	59.1	-58.2
1	3	3	16.5	-24.8
1	3	-5	47.8	-50.3
1	3	5	0.	-8.1
1	3	-7	47.9	-51.3
1	3	7	0.	12.5
1	3	-9	44.5	-42.8
1	3	9	0.	-11.4
1	3	-11	0.	-19.7
1	3	11	0.	12.7
2	3	-1	9.6	10.4
2	3	1	11.4	-5.0
2	3	-3	13.9	-18.7
2	3	3	0.	6.1
2	3	-5	47.4	-43.0
2	3	5	16.9	21.9
2	3	-7	46.1	-46.7
2	3	7	0.	21.4
2	3	-9	39.1	-37.7
2	3	-11	19.6	-22.9
2	3	-13	19.1	-18.8
3	3	-1	46.3	50.8
3	3	1	34.6	35.7
3	3	-3	0.	3.8
3	3	3	28.6	27.1
3	3	-5	9.0	13.8
3	3	5	42.3	39.3
3	3	-7	0.	5.0
3	3	-9	0.	-10.6
3	3	-11	19.4	-19.3
3	3	-13	0.	-12.0
4	3	1	29.2	43.9
4	3	-1	45.4	46.1
4	3	-3	40.3	45.6
4	3	-5	45.7	49.4
4	3	-7	22.2	20.8
4	3	-9	21.6	28.2
4	3	-11	0.	2.4
4	3	-13	0.	8.8
5	3	1	27.0	30.2
5	3	-1	17.7	22.3
5	3	-3	16.7	24.1
5	3	-5	28.6	36.3
5	3	-7	42.0	44.4
5	3	-9	41.2	41.6
5	3	-11	24.0	22.0
5	3	-13	19.6	18.7
6	3	-1	0.	8.0
6	3	1	0.	-5.0
6	3	-3	0.	3.4
6	3	-5	0.	21.1
6	3	-7	29.6	33.8
6	3	-9	0.	11.4
6	3	-11	28.1	30.6
6	3	-13	19.2	23.2
6	3	-15	16.5	17.9
0	4	2	8.0	13.7
0	4	4	28.6	24.4
0	4	6	15.0	16.6
0	4	8	0.	10.2
1	4	0	46.1	52.4
1	4	2	12.7	-13.8
1	4	-2	0.	6.2
1	4	4	0.	7.0
1	4	-4	0.	3.3
1	4	6	0.	-0.1
1	4	8	0.	6.7
1	4	10	0.	2.8
2	4	0	14.9	21.6
2	4	-2	19.3	-16.1
2	4	2	22.4	13.0
2	4	-4	11.0	14.4
2	4	4	15.8	-8.5
2	4	-6	23.3	29.6
2	4	6	0.	2.5
2	4	-8	16.3	5.8
2	4	8	19.4	-12.0
2	4	10	0.	-1.7
3	4	0	23.3	-22.1
3	4	-2	12.2	-2.6
3	4	2	0.	-0.1
3	4	-4	0.	-5.4
3	4	4	31.0	-27.7
3	4	-6	14.0	13.7
3	4	6	0.	-0.9
3	4	-8	0.	-5.0
3	4	8	0.	-3.3
3	4	-10	0.	7.1
3	4	-12	13.7	14.5
4	4	-2	0.	-9.2
4	4	-4	35.5	-34.4
4	4	-6	18.7	13.8
4	4	-8	23.8	-23.2
4	4	-10	0.	-1.6
4	4	-12	0.	3.1
5	4	0	0.	-6.7
5	4	-2	17.4	-13.4
5	4	2	19.4	-16.4
5	4	-4	0.	-8.5
5	4	-6	0.	-4.3
5	4	-8	25.3	-23.7
5	4	-10	0.	-7.9
5	4	-12	0.	-1.8
5	4	-14	0.	-3.7
6	4	0	0.	2.7
6	4	-2	19.2	-15.8
6	4	-4	0.	-0.7
6	4	-6	18.6	-18.8
6	4	-8	0.	-5.4
6	4	-10	0.	-14.6
6	4	-12	0.	-2.1
7	4	-8	0.	-3.8
0	5	1	73.5	72.8
0	5	3	68.7	66.2
0	5	5	43.4	42.2
0	5	7	23.8	25.5
1	5	1	25.5	34.3
1	5	-1	43.9	42.6
1	5	-3	78.3	71.7
1	5	3	24.6	21.9
1	5	-5	56.4	51.6
1	5	-7	54.5	52.7
2	5	-1	24.9	26.8
2	5	-3	20.8	18.5
2	5	-5	30.6	27.7
2	5	-7	43.0	37.5
2	5	-9	25.1	27.1
3	5	1	36.2	-36.1
3	5	-1	26.1	-26.5
3	5	3	41.5	-42.4
3	5	-3	30.6	-30.5
3	5	-5	0.	3.7
4	5	-1	44.4	-39.4
4	5	-3	47.0	-38.8
4	5	-5	47.7	-43.5
4	5	-7	39.8	-35.9
5	5	-3	34.3	-33.8
5	5	-5	41.5	-38.2
5	5	-7	35.0	-25.6
5	5	-9	45.0	-38.2
0	1	2	20.6	13.7
0	1	4	38.2	-31.3
0	1	6	30.4	-30.3
0	1	8	48.2	-52.1
0	1	10	24.6	-29.5
0	1	12	11.9	-20.9
1	1	0	76.1	-103.6
1	1	-2	10.6	-12.0
1	1	2	88.5	-98.3
1	1	-4	12.3	-11.4
1	1	4	88.9	-96.4
1	1	-6	0.	-8.0
1	1	6	36.8	-45.7
1	1	-8	0.	10.9
1	1	8	40.5	-43.4
1	1	-10	0.	4.7
1	1	10	21.5	-20.1
1	1	-12	0.	17.1
2	1	0	98.4	-108.7
2	1	-2	99.4	-92.6
2	1	2	47.5	-53.0
2	1	-4	170.1	-154.4
2	1	4	52.3	-52.8
2	1	-6	55.3	-48.9
2	1	6	22.1	-32.1
2	1	-8	38.4	-35.3
2	1	-10	16.1	-20.3
2	1	-12	0.	1.3
3	1	0	55.2	-60.1
3	1	-2	56.6	-57.7
3	1	2	51.6	-46.4
3	1	-4	81.6	-78.1
3	1	4	0.	-14.4
3	1	-6	51.5	-46.3
3	1	-8	108.4	-94.7
3	1	-10	41.9	-42.4
3	1	-12	39.1	-36.4
4	1	0	16.5	11.5
4	1	-2	34.7	-40.7
4	1	-4	29.3	-34.1
4	1	-6	71.5	-65.7
4	1	-8	56.4	-52.4
4	1	-10	32.0	-25.4
4	1	-12	52.4	-53.1
4	1	-14	17.0	-17.7
5	1	0	15.8	24.0
5	1	-2	14.6	17.4
5	1	-4	31.3	30.9
5	1	-6	14.2	-9.2
5	1	-8	0.	5.4
5	1	-10	28.5	-35.3
5	1	-12	24.8	-27.5
6	1	0	30.2	20.5
6	1	-2	37.3	35.3
6	1	-4	22.7	22.1
6	1	-6	22.6	25.3
6	1	-8	28.4	30.2
6	1	-10	0.	2.5
6	1	-12	0.	19.4
0	2	1	41.5	-46.8
0	2	3	29.5	-33.4
0	2	5	0.	-7.2
0	2	7	30.9	-31.4
0	2	9	21.1	-16.0
1	2	-1	22.2	-21.4
1	2	1	41.1	-45.5
1	2	-3	60.2	-60.0
1	2	3	35.6	-38.9
1	2	-5	15.9	-17.2
1	2	5	36.0	-40.7
1	2	-7	20.2	24.0
1	2	7	24.0	-29.9
1	2	-9	0.	-1.4
1	2	9	0.	-24.2
1	2	-11	0.	14.6
1	2	11	0.	-4.0
2	2	-1	58.5	-61.6
2	2	1	46.0	-56.3
2	2	-3	60.0	-59.4
2	2	3	40.2	-47.5
2	2	-5	15.7	-13.7
2	2	5	13.1	-17.4
2	2	-7	50.1	-50.6
2	2	7	0.	-10.1
2	2	-9	19.1	-17.7
2	2	9	0.	-8.7
2	2	-11	0.	-4.5
2	2	-13	0.	-5.0
3	2	-1	35.5	-42.8
3	2	1	10.8	-7.9
3	2	-3	36.3	-39.8
3	2	3	12.7	-16.1
3	2	-5	62.8	-61.4
3	2	5	0.	-6.2
3	2	-7	50.8	-48.3
3	2	-9	18.9	-17.4
3	2	-11	26.3	-29.8
3	2	-13	0.	-11.0
4	2	-1	11.6	-10.4
4	2	1	13.0	-10.5
4	2	-3	0.	4.1
4	2	3	17.9	14.6
4	2	-5	40.0	-39.9
4	2	-7	0.	-5.0
4	2	-9	43.1	-43.4
4	2	-11	26.3	-26.8
4	2	-13	0.	-14.2
5	2	-1	38.9	31.6
5	2	1	0.	8.9
5	2	-3	12.9	7.2
5	2	-5	0.	-3.9
5	2	-7	0.	3.1
5	2	-9	14.3	-11.0
5	2	-11	10.9	-3.8
5	2	-13	15.6	-18.4
6	2	1	15.7	14.7
6	2	-1	15.4	13.3
6	2	3	0.	4.6
6	2	-3	0.	12.5
6	2	-5	22.8	28.1
6	2	-7	17.9	13.6
6	2	-9	18.5	20.0
6	2	-11	0.	-5.6
0	3	2	13.5	-12.8
0	3	4	36.0	30.9
0	3	6	0.	9.9
0	3	8	17.9	18.9
1	3	0	71.1	76.9
1	3	-2	14.7	4.8
1	3	2	22.5	7.1
1	3	-4	14.7	10.2
1	3	4	59.1	59.2
1	3	-6	0.	-5.1
1	3	6	36.7	36.9
1	3	-8	0.	-0.2
1	3	8	0.	17.0
1	3	-10	0.	-8.7
1	3	10	19.6	16.4
1	3	-12	0.	-9.1
1	3	12	0.	4.5
2	3	0	58.2	66.0
2	3	-2	42.0	50.2
2	3	2	17.9	35.5
2	3	-4	50.7	51.7
2	3	4	21.9	22.7
2	3	-6	32.3	32.6
2	3	6	18.3	17.6
2	3	-8	35.9	36.2
2	3	-10	13.3	-7.3
2	3	-12	0.	11.0
2	3	-14	0.	-3.4
3	3	0	13.1	20.2
3	3	-2	33.7	37.1
3	3	2	21.6	21.7
3	3	-4	40.3	39.4
3	3	4	0.	15.8
3	3	-6	39.9	39.4
3	3	6	0.	4.7
3	3	-8	42.4	34.9
3	3	-10	18.5	22.2
3	3	-12	19.9	23.2
4	3	0	0.	13.0
4	3	2	0.	-4.7
4	3	-2	17.8	13.4
4	3	-4	24.6	29.4
4	3	-6	21.2	22.3
4	3	-8	23.5	27.8
4	3	-10	32.2	34.5
4	3	-12	0.	8.1
5	3	0	0.	-17.4
5	3	-2	0.	-9.6
5	3	2	0.	-10.7
5	3	-4	0.	-6.3
5	3	-6	0.	-1.7
5	3	-8	0.	14.8
5	3	-10	0.	9.3
5	3	-12	0.	9.8
6	3	0	0.	-14.7
6	3	-2	0.	-2.2
6	3	-4	22.9	-28.0
6	3	-6	0.	-8.0
6	3	-8	0.	-9.4
6	3	-10	19.7	-11.3
6	3	-12	0.	3.3
6	3	-14	0.	2.5
0	4	1	12.5	-6.3
0	4	3	31.4	28.3
0	4	5	31.3	36.0
0	4	7	23.5	25.7
1	4	1	19.5	36.9
1	4	-1	67.0	64.7
1	4	3	65.4	67.1
1	4	-3	28.6	29.0
1	4	-5	0.	2.2
1	4	5	47.8	49.0
1	4	7	40.3	39.8
1	4	9	27.5	22.2
2	4	-1	84.5	87.4
2	4	1	58.3	63.9
2	4	-3	55.1	52.9
2	4	3	32.0	41.8
2	4	-5	66.6	63.0
2	4	5	34.3	35.8
2	4	-7	36.5	38.4
2	4	7	0.	12.3
2	4	9	0.	11.4
3	4	-1	22.0	35.7
3	4	1	40.8	36.3
3	4	-3	54.3	56.8
3	4	3	0.	11.6
3	4	-5	65.5	67.6
3	4	5	18.9	17.2
3	4	-7	47.7	51.2
3	4	7	0.	-2.4
3	4	-9	34.9	42.3
3	4	-11	23.6	31.9
3	4	-13	18.7	17.0
4	4	-1	0.	7.1
4	4	-3	35.6	38.1
4	4	-5	14.8	10.6
4	4	-7	42.3	42.6
4	4	-9	35.6	37.4
4	4	-11	27.2	34.3
4	4	-13	23.2	24.9
5	4	-1	17.9	-16.9
5	4	1	26.9	-25.0
5	4	-3	0.	-12.6
5	4	-5	20.5	-21.9
5	4	-7	0.	17.6
5	4	-9	13.1	12.4
5	4	-11	13.7	8.4
5	4	-13	18.8	21.0
6	4	-1	0.	-13.3
6	4	1	23.5	-17.8
6	4	-3	23.2	-24.8
6	4	-5	22.8	-27.4
6	4	-7	18.7	-16.7
6	4	-9	0.	-17.6
6	4	-11	0.	-12.1
0	5	2	16.5	-15.6
0	5	4	0.	11.4
0	5	6	21.7	13.0
1	5	0	26.2	18.1
1	5	2	0.	-7.1
1	5	-2	0.	3.9
1	5	-4	22.0	-12.2
1	5	-6	0.	10.2
2	5	-2	17.2	-0.1

where X', Y, Z' are coordinates in Å referred to orthogonal axes a, b and c^*. The maximum displacement of the four atoms from the plane (Table 2) is 0·03 Å, but N(2) is displaced by 0·32 Å. The second description is in terms of the plane through C(3), C(4), C(5), which has equation

$$0{\cdot}0087X' + 0{\cdot}9689Y + 0{\cdot}2473Z' = 0{\cdot}9639. \qquad (2)$$

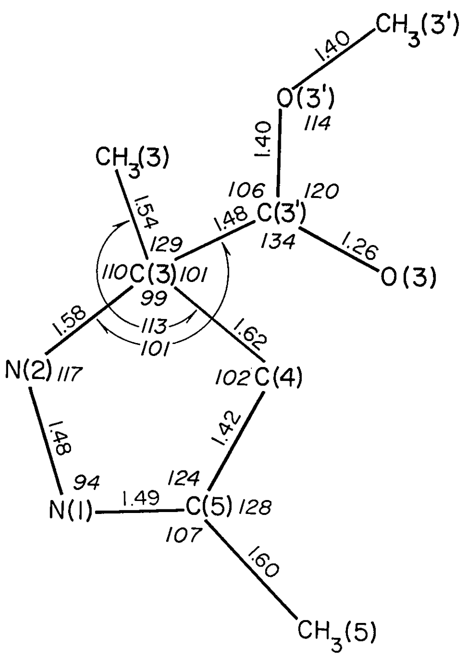


Fig. 2. Bonds lengths (Å) and valency angles (°).

N(1) and N(2) are displaced in opposite directions from this plane by 0·13 Å and 0·22 Å respectively (Table 2).

All the shorter intermolecular contacts are given in Table 3, and the packing of the molecules is shown in Fig. 3.

Discussion

The results of the present analysis indicate clearly that the compound studied is not a simple hydrobromide of 3-methoxycarbonyl-*trans*-3,5-dimethyl-Δ^1-pyrazoline. From an initial examination of the general shape of the molecule it is clear that the five-membered ring is not planar, but is best described in terms of either

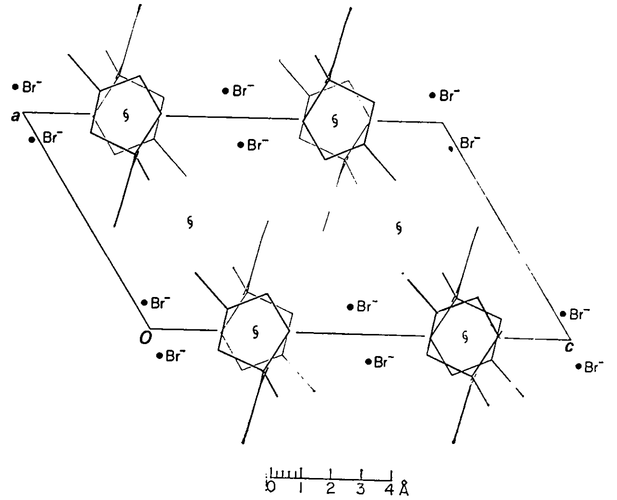


Fig. 3. Projection of the structure along b, illustrating the molecular packing.

Table 2. *Final coordinates (fractional) with standard deviations* (Å), *isotropic* (Å^2) *and anisotropic* (x 10^4) *thermal parameters, and deviations* (Δ) *from the best ring planes*

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Br^-	0·1222	0·2002	0·0180	0·006	0·006	0·006
N(1)	−0·1812	0·0642	0·1647	0·043	0·048	0·041
N(2)	−0·0067	0·0271	0·1662	0·032	0·035	0·029
C(3)	0·1834	0·0136	0·2867	0·042	0·045	0·041
C(4)	0·0907	−0·0073	0·3627	0·049	0·047	0·045
C(5)	−0·1059	0·0170	0·2821	0·049	0·051	0·043
$CH_3(3)$	0·2971	−0·1053	0·2878	0·035	0·039	0·033
$CH_3(5)$	−0·2740	0·0339	0·3061	0·055	0·061	0·047
C(3′)	0·2456	0·1510	0·3130	0·038	0·040	0·035
O(3)	0·1625	0·2575	0·2735	0·032	0·046	0·031
O(3′)	0·4395	0·1482	0·3997	0·034	0·036	0·033
$CH_3(3')$	0·5212	0·2712	0·4393	0·047	0·039	0·053

Atom	B	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}	Δ_1(Å)	Δ_2(Å)
Br^-	5·05	309	−55	204	139	−11	75	—	—
N(1)	9·50	464	123	386	278	147	136	**+0·016**	+0·132
N(2)	2·05	195	18	112	188	−7	31	−0·324	−0·221
C(3)	3·58	182	222	117	200	−33	62	**−0·018**	**0**
C(4)	3·68	190	119	93	176	4	75	**+0·031**	**0**
C(5)	5·86	364	151	248	333	−120	68	**−0·031**	**0**
$CH_3(3)$	2·32	142	160	117	91	−21	42	−1·170	−1·177
$CH_3(5)$	6·24	392	111	234	459	−13	71	+0·201	+0·224
C(3′)	2·82	200	134	148	154	−1	42	+1·430	+1·451
O(3)	5·95	400	−116	222	551	14	71	—	—
O(3′)	8·92	408	−160	312	295	63	139	—	—
$CH_3(3')$	5·20	296	−136	136	20	−49	134	—	—

the plane through the four atoms N(1), C(3), C(4), C(5), with N(2) displaced −0·32 Å from this plane, or the plane through the three carbon atoms, with N(1) and N(2) displaced in opposite directions. In either case the deviation of $CH_3(3)$ from the plane is −1·2 Å, and of $CH_3(5)$ +0·2 Å, so that the methyl groups appear to be *trans*. However, while the $CH_3(3)$ displacement is reasonable for an atom bonded to a tetrahedral atom in the ring, the displacement of $CH_3(5)$ is much smaller and indicates (as do the bond angles discussed later) that C(5) is a trigonal carbon atom. In fact the small displacement of $CH_3(5)$ is probably a result of crystal packing forces (discussed later). There is therefore no question of *cis–trans* isomerism in the hydrobromide, so that the analysis has not resolved the original problem of the configuration of the parent Δ^1-pyrazoline.

The next features which must be studied are the bond distances and valency angles. These have not been determined very accurately, as a result of the presence of the bromine atom, of possible absorption errors, and of the rather small number of observed reflexions. However it is very obvious, even with this limited accuracy, that there is no double bond in the ring. The N(1)–N(2) bond for example measures 1·48 ± 0·06 Å, significantly longer than the double-bond distance. The shortest ring bond is C(4)–C(5), which is 1·42 ± 0·06 Å; even this is longer than the double-bond distance, and in any case chemical considerations rule out the possibility of a double bond in this position. The sum of the angles at C(5) is 359° (Fig. 2), indicating as do the displacements from planarity (the two features are of course related) that C(5) is a trigonal atom.

It is now possible to deduce the structure of the cation. Since it has been established during the refinement that N(1) carries some positive charge, and since N(1)–N(2) is not a double bond, and since C(5) is trigonal, we may write (VI*a*) as one possible structure for the cation. This structure cannot be completely correct, since a C(5)–N(1) double bond has already been ruled out. The final clue is that C(5) has a relatively low density (Fig. 1) and its temperature factor is somewhat higher than those of C(3) and C(4) (Table 2); these facts suggest that C(5) carries some of the positive charge, so that the final structure is a resonance hybrid of the two canonical forms (VI*a*) and (VI*b*). (VI*b*) is an unusual formulation, but it is supported by the various points mentioned above, and by one further piece of evidence: C(5) is involved in an unusually short intermolecular contact, 2·76 Å (to O(3) of a molecule related by a screw axis, Table 3), a distance about 0·3 Å shorter than the usual van der Waals distance (3·1 Å). This distance is in accord with attraction between the partial positive charge on C(5) and the relatively negative oxygen atom.

The reaction of 3-methoxycarbonyl-*trans*-3,5-dimethyl-Δ^1-pyrazoline with hydrogen bromide must involve an initial rearrangement to a Δ^2-pyrazoline (V), a chemically reasonable acid rearrangement process, followed by formation of the hydrobromide. Conclusive evidence for this rearrangement was obtained by treating the hydrobromide with sodium bicarbonate; the product was different from the original Δ^1-pyrazoline, and its nuclear magnetic resonance spectrum was consistent with structure (V) (Chiu & McGreer, 1965).

Table 3. *Shorter intermolecular distances*

All distances ≤4 Å between molecule 1 and neighbouring molecules were calculated, but only the more significant contacts are listed.

Molecule			
1 at	x,	y,	z
2 at	$-x$,	$-y$,	$-z$
3 at	$-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
4 at	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$
5 at	$1+x$,	y,	z
6 at	$1-x$,	$-y$,	$1-z$

Atom (in molecule 1)	to Atom	in Molecule	d
Br^-	N(2)	1	3·31 Å
Br^-	N(1)	1	4·24
Br^-	O(3)	1	3·44
Br^-	C(3′)	1	3·70
Br^-	N(2)	2	3·22
Br^-	N(1)	2	3·93
Br^-	$CH_3(3)$	2	3·91
O(3)	Br^-	4	3·62
O(3)	N(1)	3	3·26
O(3)	N(2)	3	3·36
O(3)	$CH_3(5)$	3	3·36
O(3)	C(5)	3	2·76
O(3)	C(4)	3	3·10
O(3′)	$CH_3(5)$	5	3·47
$CH_3(3')$	$CH_3(3)$	6	3·67
N(1)	$CH_3(3)$	3	3·70

All the other bond distances and valency angles in the molecule are relatively normal. The angles in the ring are somewhat irregular, but this is not too surprising in such an unusual ring system. The external angles, and the bond lengths and angles in the methoxycarbonyl group do not differ much from the usual values.

The intermolecular distances require some special comment. The shortest contact between molecules is the C(5) ··· O(3) contact of 2·76 Å discussed above, and this short distance results in several other short approaches involving O(3) in the range 3·1 – 3·4 Å (Table 3). One of these short contacts is between O(3) and $CH_3(5)$, where the distance is 3·36 Å; if $CH_3(5)$ lay in the best ring plane, this distance would be about 0·2 Å shorter, so that it seems very likely that the slight non-planarity at C(5) discussed above is a result of crystal packing forces. The shortest distances involving the bromide ion are not to N(1) or C(5) but to N(2), there being two Br^- ··· N(2) contacts, 3·22 Å and 3·31 Å (Table 3). One of these distances probably represents a N–H ··· Br^- hydrogen bond (none of the evidence cited above for the structure of the cation is in accord with two hydrogen atoms, and therefore a positive charge, on N(2), so that N(2) cannot form two hydrogen bonds). The bond angles involved are:

Br_{I}^- ··· N(2)–N(1) = 83° Br_{II}^- ··· N(2)–N(1) = 118°
Br_{I}^- ··· N(2)–C(3) = 114° Br_{II}^- ··· N(2)–C(3) = 119°

where Br_I^- is the standard bromide ion (at x, y, z), and $\mathrm{Br}_\mathrm{II}^-$ is at ($\bar{x}$, $\bar{y}$, $\bar{z}$). The equal angles involving $\mathrm{Br}_\mathrm{II}^-$, and the very small angle (83°) involving Br_I^-, suggest that $\mathrm{Br}_\mathrm{II}^-$ is hydrogen-bonded to N(2), distance 3·22 Å. The $\mathrm{Br}_\mathrm{I}^- \cdots$ N(2) distance (3·31 Å) is slightly shorter than the sum of the ionic radius of Br^- and van der Waals radius of nitrogen (3·45 Å). All the other intermolecular distances are normal; the shortest $\mathrm{Br}^- \cdots$ N(1) contact is 3·93 Å.

The authors are indebted to Dr D. E. McGreer and Mr N.W.K. Chiu for the crystal sample and for helpful discussion, to the staff of the University of British Columbia Computing Center for assistance, and to the National Research Council of Canada for financial support.

References

Chiu, N. W. K. & McGreer, D. E. (1965). Personal communication.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

McGreer, D. E., Chiu, N. W. K., Vinje, M. J. & Wong, K. C. K. (1965). In preparation.

McGreer, D. E., Morris, P. & Carmichael, G. (1963). *Canad. J. Chem.* **41**, 726.

Acta Cryst. (1965). **19**, 619

Structural Studies of Metal Dithiocarbamates.
I. The Crystal and Molecular Structure of the α Form of Nickel Diethyldithiocarbamate*

By M. Bonamico, G. Dessy†, C. Mariani‡, A. Vaciago and L. Zambonelli

Centro di Studio per la Strutturistica Chimica (CNR), Istituto di Chimica Farmaceutica e Tossicologica della Università degli Studi, Roma, Italy

(*Received* 18 *January* 1965)

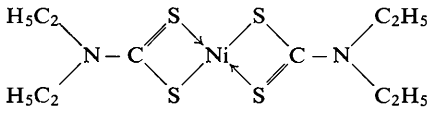
The crystal structure of the α form of nickel(II) bis(*N,N*-diethyldithiocarbamate), $[(C_2H_5)_2NCS_2]_2Ni$, at room temperature, has been determined by three-dimensional methods. There are two formula units in the monoclinic unit cell, $a = 6·189$, $b = 11·537$, $c = 11·603$ Å, $\beta = 95°\,51'$, with space group $P2_1/c$. Each nickel atom occupies a centre of symmetry with the two ligand molecules planarly coordinated through the sulphur atoms. Three-dimensional anisotropic refinement by differential Fourier synthesis (final R value, 0·101) gave the bond lengths as Ni–S = 2·20, S–C = 1·71 and C–N = 1·33 Å, proved the planarity of the ligand molecule (obviously apart from the terminal CH_3 groups), and confirmed that $\cdots S_2C=NR_2$ is an important canonical form in the structure. The shortest intermolecular nickel contact is to a carbon atom at 3·54 Å.

Introduction

The structures of metal dithiocarbamates are being investigated because of (i) the fact that most of their detailed structures are unknown, (ii) the theoretical interest arising from the sulphur-containing four-membered rings present in these compounds, (iii) their biological (antifungal) activity, (iv) the lack of correlation between structural properties and the known chemical and physical properties of these compounds (Thorn & Ludwig, 1962).

The unusual features of this class of compound became apparent from the pioneering investigations of their physical and chemical properties carried out by Livio Cambi (Cambi & Malatesta, 1937; Malatesta, 1937; Cambi, 1941; and previous references quoted therein) who called our attention to the need for structural studies.

The first compound investigated in our laboratory was nickel(II) bis(*N,N*-diethyldithiocarbamate):



with the bond orders written in the conventional way. The first structural determination of a nickel salt had been that of Peyronel (1940 *a*, *b*), who published crystal data and a qualitative structure on the di-n-propyl derivative. Preliminary work (crystal data and two-dimensional structure analysis) had also been published on nickel(II) bis(*N,N*-diethyldithiocarbamate) by several research groups (Vaciago & Fasana, 1958; Pullia & Vaciago, 1960; Vaciago, Cabrini & Mariani, 1960; Shugam & Shkol'nikova, 1958; Shugam & Levina, 1960; Franzini & Schiaffino, 1963). Accurate data on bond lengths and angles, however, were still lacking.

---

* This paper was part of communication 6·27 to the I.U.Cr. Sixth International Congress held in Rome in 1963.

† Permanent address: Istituto di Chimica Generale e Inorganica della Università degli Studi, Roma, Italy.

‡ Permanent address: Istituto di Chimica Fisica della Università degli Studi, Milano, Italy.