

reasonably explains the pronounced cleavage parallel to (001).

Molecule *i* (see Fig. 3) can form N–H···O hydrogen bonds with either of the molecules *iii* and *iv* and also with either *v* or *vi* in a disordered state. However, hydrogen-bond distances of N(1ⁱ)···O(2^{iv}) (2.84) and of N(2ⁱ)···O(1^{vi}) (2.74 Å) are slightly shorter than those of N(1ⁱ)···O(1ⁱⁱⁱ) (2.94) and N(2ⁱ)···O(2^v) (2.83 Å). Therefore it is likely that molecule *i* prefers to occupy the position in the neighbourhood of *iv* rather than of *iii*. On the other hand, an abnormally short methyl–methyl contact is found between *i* and *x* [C(5ⁱ)···C(5^x), 3.16 Å]. Molecule *i*, therefore, should prefer also to occupy the site in the neighbourhood of molecule *ix* rather than *x*. This arrangement of the molecule, with *i* situated in the neighbourhood of *iv*, *vi* and *ix*, corresponds to the space group $P2_1/n$, which must be the basic structure in an ordered state. The crystal is probably partially ordered; diffuse spots are observed at the reciprocal lattice points forbidden by the space group $C2/c: hkl$ with $h+k$ odd and $h0l$ with h and l odd.

All crystallographic computations were performed on the HITAC 5020E and 8800 computers of the Computer Centre of the University of Tokyo using the program system UNICS (Crystallographic Society of Japan, 1967; Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967).

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1,1,1-Trimethylhydrazinium 3-Carbomethoxy-5-pyrazolecarboxylate

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Abstract. $[(\text{CH}_3)_3\text{NNH}_2^+][\text{CH}_3\text{OCO}-(\text{C}_3\text{N}_2\text{H}_2)-\text{COO}^-]$, ($\text{C}_9\text{H}_{16}\text{N}_4\text{O}_4$), $M=244.16$, monoclinic, $C2/c$, $a=18.227(2)$, $b=8.019(1)$, $c=18.284(2)$ Å, $\beta=113.68(1)^\circ$, $V=2447.5$ Å³, $Z=8$, $D_x=1.325$, $D_m=1.327$ g cm⁻³. Full-matrix least-squares refinement of 1669 reflections [$I>3\sigma(I)$] collected with θ - 2θ scans on a Syntex $P2_1$ diffractometer yielded a final R of 0.043. Multiple hydrogen bonds are found between the cations and anions.

Introduction. The space group and approximate unit-cell dimensions were determined from a study carried out on a Syntex $P2_1$ diffractometer. The cell parameters were later refined using the Bragg angles of Cu $K\alpha_1$ peaks of 24 high-angle reflections measured on a GE XRD-5 diffractometer (Cu $K\alpha_1=1.54050$ Å). A crystal which measured $0.27 \times 0.31 \times 0.26$ mm perpendicular to (111), (1 $\bar{1}$ 1) and (10 $\bar{1}$), respectively, was selected for

mounting on the Syntex diffractometer. Molybdenum $K\alpha$ radiation (0.71069 Å) monochromatized by a graphite crystal was used for data collection. The θ - 2θ scan technique was employed with scans ranging from 1° below the $K\alpha_1$ peak to 1° above the $K\alpha_2$ peak and with scan rates determined in the following way. A preliminary two second count was made using the stationary-crystal-stationary-counter technique. All reflections with counts below 150 were collected at the minimum scan rate of 1° min^{-1} ; all those above 1500 were collected at the maximum rate of 5° min^{-1} ; and the remainder were collected at a rate specified by the algorithm: scan rate = $0.002963 \times \text{preliminary count} + 0.5556$. Background measurements were taken at both ends of the scan range, each for a time equal to one-half of the scan time. Four standard reflections were monitored every 46 reflections; no intensity change was observed throughout the data-collection period. In

Table 1. Atomic coordinates and thermal parameters (both $\times 10^4$) for the non-hydrogen atoms with *e.s.d.*'s in parentheses

The thermal parameters are of the form $\exp \{-[h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]\}$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	4481 (1)	4296 (3)	3529 (1)	22 (1)	126 (4)	27 (1)	-1 (2)	12 (1)	-6 (2)
C(2)	4512 (1)	3460 (3)	4195 (1)	24 (1)	150 (5)	31 (1)	0 (2)	17 (1)	2 (2)
C(3)	5296 (1)	2901 (3)	4580 (1)	26 (1)	121 (4)	26 (1)	-1 (2)	13 (1)	1 (2)
C(4)	3821 (1)	5174 (3)	2876 (1)	29 (1)	128 (4)	30 (1)	5 (2)	13 (1)	-7 (2)
C(5)	5638 (1)	1969 (3)	5330 (1)	32 (1)	134 (5)	31 (1)	-7 (2)	15 (1)	-3 (2)
C(6)	6810 (2)	714 (4)	6270 (2)	48 (1)	194 (6)	34 (1)	20 (3)	13 (1)	22 (2)
C(7)	1322 (2)	5232 (5)	2977 (2)	50 (2)	325 (9)	55 (2)	56 (3)	18 (1)	-6 (3)
C(8)	1261 (3)	3610 (5)	4085 (3)	69 (2)	297 (9)	93 (3)	-62 (4)	66 (2)	-67 (4)
C(9)	2343 (2)	5607 (4)	4323 (2)	45 (1)	204 (7)	62 (2)	-34 (3)	30 (1)	-52 (3)
N(1)	5234 (1)	4209 (2)	3553 (1)	26 (1)	153 (4)	28 (1)	5 (1)	14 (1)	13 (1)
N(2)	5747 (1)	3377 (2)	4186 (1)	27 (1)	163 (4)	29 (1)	7 (1)	13 (1)	13 (1)
N(3)	1801 (1)	4393 (2)	3747 (1)	32 (1)	174 (4)	42 (1)	-13 (2)	22 (1)	-25 (2)
N(4)	2298 (1)	3078 (3)	3641 (1)	36 (1)	164 (5)	45 (1)	-3 (2)	21 (1)	-21 (2)
O(1)	3170 (1)	5317 (2)	2941 (1)	25 (1)	236 (4)	41 (1)	13 (1)	18 (1)	7 (1)
O(2)	3974 (1)	5708 (2)	2304 (1)	36 (1)	209 (3)	35 (1)	29 (1)	21 (1)	21 (1)
O(3)	6401 (1)	1529 (2)	5512 (1)	32 (1)	178 (3)	29 (1)	12 (1)	13 (1)	16 (1)
O(4)	5284 (1)	1628 (2)	5739 (1)	46 (1)	280 (4)	47 (1)	5 (2)	31 (1)	34 (2)

total, 2810 reflections were measured in the range $4^\circ < 2\theta < 55^\circ$. Lorentz and polarization corrections were applied; no absorption correction was made. Standard deviations in the intensities, $\sigma(I)$, and in structure amplitudes, $\sigma(F_o)$, were derived from counting statistics.

The structure was solved by the symbolic addition method; the distribution of *E*'s indicated the space group to be *C2/c* and not *Cc*. The hydrogen atoms were found in a difference map. Only the 1669 reflections for which $I > 3\sigma(I)$ were used in the full-matrix least-squares refinement (*NUCLS*: J. A. Ibers's modification of *ORFLS*); they were assigned weights of $1/\sigma^2(F_o)$. Final cycles refined all positional parameters, anisotropic thermal parameters of the non-hydrogen atoms, and isotropic thermal parameters of the hydrogen atoms. At convergence; the value of *R*, $\sum |F_o| - |F_c| / \sum |F_o|$, was 0.043; for all 2810 reflections, *R* = 0.079. Extinction effects were not evident. The estimated

Table 2. Atomic coordinates ($\times 10^3$) and isotropic thermal parameters (\AA^2) for the hydrogen atoms

The hydrogen atoms of the four methyl groups are numbered according to the carbon atom to which they are bonded, e.g. H(1,6) is hydrogen atom 1 attached to carbon atom C(6).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	406 (1)	328 (2)	433 (1)	2.6 (0.4)
H(2)	541 (1)	471 (3)	321 (1)	5.6 (0.6)
H(3)	261 (1)	361 (1)	338 (1)	5.5 (0.6)
H(4)	192 (1)	230 (3)	326 (2)	5.7 (0.6)
H(1,6)	735 (1)	41 (3)	630 (1)	6.3 (0.7)
H(2,6)	683 (1)	145 (3)	671 (1)	6.6 (0.7)
H(3,6)	652 (1)	-38 (3)	629 (1)	6.5 (0.7)
H(1,7)	92 (2)	427 (4)	259 (2)	10.9 (1.1)
H(2,7)	172 (2)	574 (4)	279 (2)	10.2 (1.1)
H(3,7)	100 (1)	612 (3)	307 (1)	8.2 (0.8)
H(1,8)	94 (1)	454 (3)	416 (1)	6.9 (0.8)
H(2,8)	160 (2)	308 (4)	459 (2)	10.9 (1.4)
H(3,8)	93 (2)	277 (4)	369 (2)	9.6 (1.0)
H(1,9)	265 (2)	499 (3)	484 (2)	8.8 (1.0)
H(2,9)	274 (1)	602 (3)	410 (1)	6.7 (0.7)
H(3,9)	201 (1)	653 (3)	439 (1)	5.6 (0.6)

standard deviation in an observation of unit weight was 3.0. The largest peak in the final difference Fourier map, approximately 0.2 e \AA^{-3} , was located at oxygen atom O(1). For the non-hydrogen atoms, the atomic scattering factors of Cromer & Waber (1965) were used;

Table 3. Bond distances (\AA) and angles ($^\circ$) for 1,1,1-trimethylhydrazinium 3-carbomethoxy-5-pyrazolecarboxylate with *e.s.d.*'s in parentheses

For the anion		For the cation	
C(1)-C(2)	1.371 (3)	C(7)-N(3)	1.487 (4)
C(1)-C(4)	1.489 (3)	C(8)-N(3)	1.496 (5)
C(1)-N(1)	1.359 (3)	C(9)-N(3)	1.483 (4)
C(2)-C(3)	1.390 (3)	N(3)-N(4)	1.453 (3)
C(2)-H(1)	0.96 (2)	N(4)-H(3)	0.97 (2)
C(3)-C(5)	1.465 (3)	N(4)-H(4)	0.99 (2)
C(3)-N(2)	1.347 (3)		
C(4)-O(1)	1.245 (3)	For interionic hydrogen bonds	
C(4)-O(2)	1.262 (3)	O(1)···H(3)	2.06 (2)
C(5)-O(3)	1.341 (3)	O(2)···H(2)	1.90 (2)
C(5)-O(4)	1.200 (3)	O(2)···H(4)	2.00 (2)
C(6)-O(3)	1.441 (3)		
N(1)-N(2)	1.338 (3)	For the cation	
N(1)-H(2)	0.91 (2)	C(7)-N(3)-C(8)	110.4 (3)
		C(7)-N(3)-C(9)	110.2 (2)
		C(7)-N(3)-N(4)	111.3 (2)
		C(8)-N(3)-C(9)	110.0 (3)
		C(8)-N(3)-N(4)	107.4 (2)
		C(9)-N(3)-N(4)	107.4 (2)
		N(3)-N(4)-H(3)	105 (1)
		N(3)-N(4)-H(4)	105 (1)
		H(3)-N(4)-H(4)	108 (2)
		For interionic hydrogen bonds	
		C(4)-O(1)···H(3)	128 (1)
		C(4)-O(2)···H(2)	130 (1)
		C(4)-O(2)···H(4)	104 (1)
		N(1)-H(2)···O(2)	167 (2)
		N(4)-H(3)···O(1)	164 (2)
		N(4)-H(4)···O(2)	165 (2)

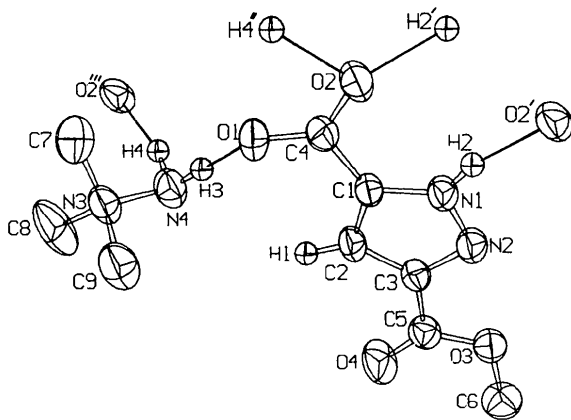


Fig. 1. Drawing of a pair of ions showing the atom-numbering scheme and the hydrogen bonds (narrow lines).

those of Stewart, Davidson & Simpson (1965) were used for the hydrogen atoms. The final positional and thermal parameters are given in Tables 1 and 2.

Discussion. Synthesis of compounds containing both an acid and an ester group is somewhat tedious, particularly when the functional groups necessary for the formation of an anhydride, a common precursor, are not vicinal. Dr J. Nematollahi of the College of Pharmacy at the University of Texas at Austin has developed a new and facile method for the synthesis of acid esters consisting of monodemethylation of a dimethyl ester with 1,1-dimethylhydrazine and subsequent conversion of the resulting 1,1,1-trimethylhydrazinium ester to the corresponding acid ester. The present crystallographic investigation was undertaken to confirm the above synthesis.

Most bond distances and angles are listed in Table 3 following the atom-numbering scheme shown in Fig. 1. Hydrogen atoms of the four methyl groups have not been included in the table or the Figure; it suffices to say the C-H bond distances varied from 0.97 to 1.10 Å while no angle deviated by more than 3σ from the tetrahedral value. Comparison of the pyrazole ring of this compound with the structure of pyrazole itself (Berthou, Elguero & Rérat, 1970; Larsen, Lehmann, Sotofte & Rasmussen, 1970) and with recent structures of substituted pyrazoles (Seeman, McGandy & Rosenstein, 1972; Lapasset & Falgueirettes, 1972) indicates general agreement of the bond distances and angles including the rather non-uniform angles around the ring and the angles made by the substituents bonded to the ring. It should be noted however that unlike

the structure of pyrazole itself, the ring here shows small differences in the two C-N distances, 1.359 and 1.347 Å, and the two C-C distances, 1.371 and 1.390 Å. This is probably a reflection of the substitution.

The pyrazole ring is planar with C(3) having the largest deviation, +0.005 Å. Carbon atoms C(4) of the carboxylate group and C(5) of the ester group deviate from the ring plane by only +0.001 and -0.025 Å, respectively. Rotations of 6.2° about the C(1)-C(4) bond and 5.3° about the C(3)-C(5) bond have caused the oxygen atoms of these groups to be slightly out of the ring plane.

The N-N bond, 1.453 Å, in the 1,1,1-trimethylhydrazinium cation appears to be intermediate in value between that found in the hydrazinium ion itself, 1.436 Å (Jönsson & Liminga, 1971; Braibanti, Manotti-Lanfredi, Tiripicchio & Logiudice, 1969), and that found in 1,1,1-trimethylhydrazinium inner salts, 1.471 and 1.470 Å (Cameron, Hair, Morris & Hawley, 1971).

Fig. 1 shows the hydrogen-bonding interactions; the bonds are nearly linear with N-H...O angles of 164, 165, and 167° . The difference in the C(4)-O(1) and C(4)-O(2) bond lengths, 1.245 vs. 1.262 Å, is undoubtedly related to the different hydrogen-bonding environments of the two oxygen atoms. Hydrogen atom H(2) was located as bonding to N(1) and not to N(2).

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