The Crystal and Molecular Structure of 7-Acetyl-3,5,5,9,9-pentamethyl-1,6-diaza-bicyclo[4.3.0]nona-3,7-dien-2-one

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An X-ray crystallographic analysis was carried out to find the chemical structure of the compound $C_{14}H_{20}N_2O_2$ ($M_r = 248 \cdot 31$), formed by the photolysis of 5-acetyl-3H-pyrazole. The crystals are orthorhombic, *Pbca*, with $a = 14 \cdot 757$, $b = 10 \cdot 680$, $c = 17 \cdot 383$ Å (all $\pm 0 \cdot 003$ Å); $Z = 8$ for $R_{calc} = 1 \cdot 204$, $\rho_{meas} = 1 \cdot 22$ g cm^{-3}. The structure was determined from three-dimensional counter data with a symbolic addition procedure, and refined by the least-squares method to $R = 0 \cdot 0881$ for 2012 reflexions. In the 1,6-diazabicyclo[4.3.0]nonadiene system found in the molecule, the five-membered ring is nearly planar and the six-membered ring considerably folded. The two N atoms are stereochemically different, one is in approximately tetrahedral coordination, and the other planar (amine and amide-like respectively).

Introduction

The irradiation of 5-acetyl-3H-pyrazole (I) was carried out with a view to obtaining the α-diazoketone (II). It provided a good opportunity for studying the partition between carbenoid decomposition and Wolff rearrangement in the photolysis of α-diazoketones. Photolysis of (I) in ether gave a mixture of several volatile products and a yellow solid, $C_{14}H_{20}N_2O_2$ (m.p. 137·4–139°C), which had $\lambda_{max.} = 312 \cdot 5$ nm (ϵ 1880) in n-hexane. The NMR spectrum of the solid indicated the presence of six methyl groups, two vinylic H atoms and two unsaturated carbonyl groups. It seemed probable that this compound was a product of [4 + 2] cycloaddition of the vinylketene (III) to the starting material (I). There were four possible structures for a [4 + 2] cycloadduct of (I) and (III) (Day & McDonald, 1970), two of which possess two vinylic H atoms. The compound was therefore subjected to X-ray crystallographic analysis to determine its actual structure.

(I)   (II)   (III)

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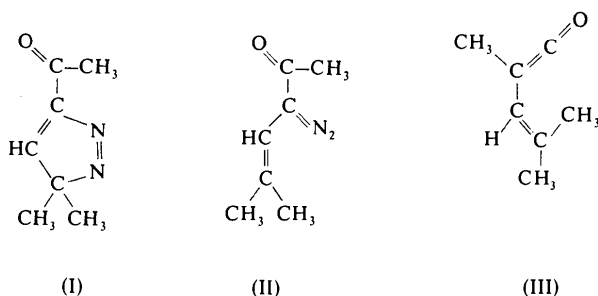
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Experimental

The crystals used for the X-ray measurements were prepared by Drs A. C. Day and A. N. McDonald of the Dyson Perrins Laboratory. They were pale-yellow, elongated prisms with well formed faces, grown from n-hexane. Rotation and equi-inclination Weissenberg photographs were taken for all three crystallographic axes from zero to second layer.

Integrated intensities for the reflexions were measured to a Bragg angle of 78° on a computer-controlled Hilger & Watts four-circle diffractometer with θ–2θ and ω scans. The reflexions were measured with a 1·0° scan at a scanning speed of 1° min^{-1}, with 50 steps and background measurements of 20 s at both sides. The strongest reflexions were corrected empirically for dead-time of the counter used. Lorentz–polarization factors were applied and the data were corrected empirically for absorption (North, Phillips & Mathews, 1968). Of the 2482 measured structure factors, 2012 which had values above 4σ were used in the structure analysis.

Structure determination and refinement

The symbolic addition procedure for centrosymmetric crystals (Karle & Karle, 1963, 1966) was used, working initially by hand to determine the phases of 133 reflexions of high $|E|$ value. The reflexions $\bar{1},\bar{2},17$, $12,3,\bar{8}$ and $9,2,10$ were assigned positive signs to fix the origin of the unit cell. The sign of $0,0,16$ was found to be positive by Σ_1 relations and the signs of $10,2,12$ and $11,4,4$ were represented by the symbols A and B. 133 signs with probabilities greater than $0 \cdot 9975$ were determined. From two possible solutions, the more consis-

tent was correct with $A \equiv +$ and $B \equiv -$. A set of signed E's obtained that way was used for calculating a Fourier synthesis. The synthesis had 14 large peaks corresponding to the non-hydrogen atoms of both rings; the substituents to the five-membered ring [C(10), C(11), C(16) and O(17)] were lacking.

The whole process was repeated with a symbolic addition system developed in our laboratory (Hodder, Prout & Rollett, 1970). 384 signs were determined and all 18 non-hydrogen atoms were clearly visible on the following E map. The trial structure was refined by isotropic procedures with large block-diagonal approximations to the full normal matrix. The H atoms were located from a difference Fourier synthesis after three cycles of isotropic refinement. The refinement was

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *with standard deviations in parentheses*

	x	y	z
N(1)	2841 (2)	3430 (3)	581 (1)
N(6)	3218 (2)	3403 (2)	1355 (1)
C(2)	1948 (2)	3646 (3)	497 (2)
C(3)	1497 (2)	4243 (3)	1161 (2)
C(4)	2007 (2)	4759 (4)	1709 (2)
C(5)	3024 (2)	4614 (3)	1752 (2)
C(7)	4134 (2)	3055 (3)	1219 (2)
C(8)	4313 (2)	2833 (3)	480 (2)
C(9)	3488 (2)	3000 (3)	−13 (2)
C(10)	3615 (2)	3984 (4)	−643 (2)
C(11)	3189 (3)	1749 (4)	−361 (2)
C(12)	486 (2)	4341 (4)	1138 (2)
C(13)	3496 (3)	5745 (4)	1381 (2)
C(14)	3283 (3)	4502 (4)	2599 (2)
C(15)	4748 (2)	2682 (3)	1855 (2)
C(16)	5740 (3)	2908 (5)	1743 (3)
O(17)	4458 (2)	2174 (3)	2430 (2)
O(18)	1554 (2)	3469 (3)	−124 (2)

Table 2. *Thermal parameters of non-hydrogen atoms* ($\times 10^3$) *with estimated standard deviations in parentheses*

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
N(1)	37 (1)	51 (2)	33 (1)	−6 (2)	−7 (2)	6 (2)
N(6)	40 (1)	46 (1)	33 (1)	−3 (2)	−5 (2)	3 (2)
C(2)	43 (2)	46 (2)	42 (2)	−2 (3)	−15 (3)	−3 (3)
C(3)	42 (2)	48 (2)	46 (2)	3 (3)	7 (3)	0 (3)
C(4)	45 (2)	51 (2)	47 (2)	−6 (3)	2 (3)	5 (3)
C(5)	50 (2)	46 (2)	40 (2)	−12 (3)	−4 (3)	1 (3)
C(7)	40 (2)	43 (2)	41 (2)	2 (3)	−6 (3)	1 (3)
C(8)	43 (2)	56 (2)	40 (2)	−3 (3)	0 (3)	2 (3)
C(9)	50 (2)	53 (2)	34 (2)	−6 (3)	0 (3)	4 (3)
C(10)	65 (3)	77 (3)	46 (2)	27 (4)	14 (4)	6 (4)
C(11)	58 (2)	62 (2)	53 (2)	−37 (4)	−7 (3)	8 (4)
C(12)	39 (2)	73 (3)	71 (3)	7 (4)	−1 (3)	−3 (4)
C(13)	58 (2)	48 (2)	69 (3)	−7 (4)	−7 (4)	−16 (3)
C(14)	70 (3)	77 (3)	45 (2)	−29 (4)	−21 (4)	22 (4)
C(15)	53 (2)	46 (2)	43 (2)	3 (3)	−11 (3)	5 (3)
C(16)	46 (2)	91 (3)	66 (3)	9 (5)	−27 (4)	5 (4)
O(17)	67 (2)	75 (2)	53 (2)	37 (3)	−14 (3)	−4 (3)
O(18)	49 (1)	70 (2)	51 (1)	−18 (3)	−28 (2)	6 (2)

Table 3. *Fractional atomic coordinates of hydrogen atoms* ($\times 10^3$) *with standard deviations in parentheses*

Atom	Atom bonded to	x	y	z	B
H(29)		3 (5)	512 (8)	96 (4)	24 (4)
H(30)	C(12)	15 (3)	345 (2)	124 (2)	5 (1)
H(31)		35 (4)	471 (6)	56 (2)	9 (2)
H(21)	C(4)	174 (3)	537 (3)	216 (2)	4 (1)
H(32)		341 (3)	575 (4)	76 (1)	4 (1)
H(33)	C(13)	421 (1)	567 (4)	152 (3)	6 (1)
H(34)		323 (3)	659 (3)	166 (3)	7 (2)
H(35)		401 (1)	451 (5)	269 (3)	6 (2)
H(36)	C(14)	303 (3)	363 (2)	284 (2)	5 (1)
H(37)		307 (3)	532 (3)	292 (2)	5 (2)
H(22)	C(8)	495 (1)	250 (3)	25 (2)	4 (1)
H(23)		297 (2)	412 (4)	−94 (2)	5 (1)
H(24)	C(10)	407 (3)	366 (4)	−109 (2)	6 (1)
H(25)		386 (3)	485 (2)	−39 (2)	6 (1)
H(26)		267 (2)	143 (4)	−79 (2)	7 (1)
H(27)	C(11)	257 (2)	179 (5)	−69 (3)	8 (2)
H(28)		309 (3)	104 (3)	8 (2)	6 (1)
H(38)		587 (4)	390 (2)	168 (3)	9 (2)
H(39)	C(16)	599 (4)	246 (5)	122 (2)	10 (2)
H(40)		610 (3)	261 (4)	226 (2)	6 (2)

then continued in an anisotropic mode for a further four cycles, when it converged at an R of 0·081. As the main purpose of the work (*i.e.* distinguishing between several possible structures) was reached, no further attempts to lower the R value were undertaken. The weighting scheme used was an empirical one: $w^{1/2} = 1/\{1 + [(|F_o| - P_1)/P_2]^2\}$, where parameters P_1 (25·4) and P_2 (36·2) were chosen in such a way as to minimize the variation of $w(|F_o| - |F_c|)^2$ with F_o. The thermal vibration of each H was set equal to that of the C atom to which it was attached. Table 1 lists the atomic coordinates of non-hydrogen atoms and Table 2 gives thermal parameters of those atoms. Table 3 gives positional and thermal parameters of all H atoms.*

Computations

All calculations were performed on the Oxford University KDF-9 computer with programs written by J. S. Rollett, E. Dodson, O. J. R. Hodder and G. Ford. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). All figures were drawn with the plotting program *STEP3*, written by Dr R. Carruthers.
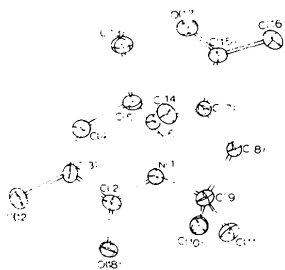
Fig. 1. Thermal ellipsoids (probability 30%) in one molecule and atomic nomenclature.
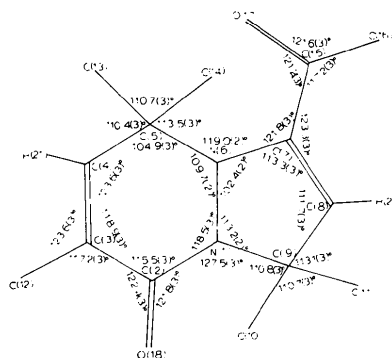
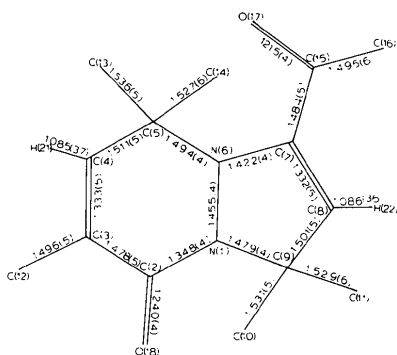Fig. 2. Bond lengths (Å). Estimated standard deviations are given in parentheses for the last digit listed.

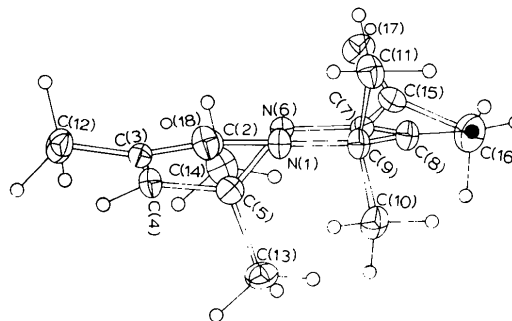Fig. 3. Bond angles (°). Estimated standard deviations are given in parentheses for the last digit listed.

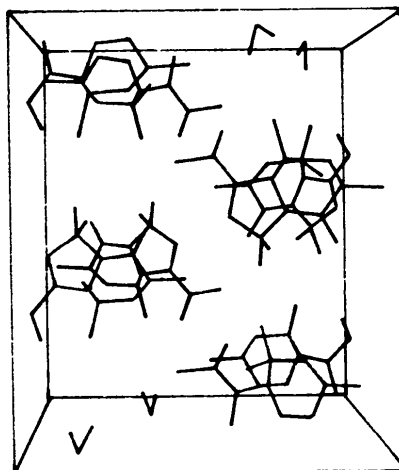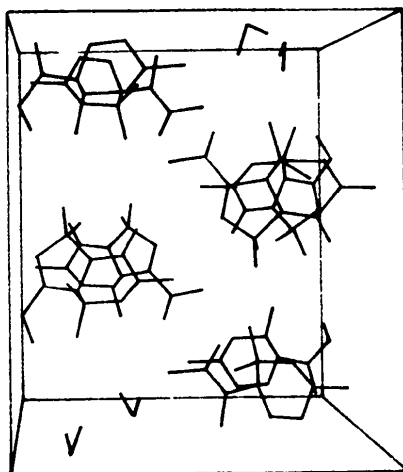Fig.4. Conformation of the molecule as seen along the plane of the five-membered ring.

Fig. 5. A stereo view of the packing in the $C_{14}H_{20}N_2O_2$ crystals. Axial directions are $a \rightarrow$, $c\uparrow$ and b out from the plane of the paper.
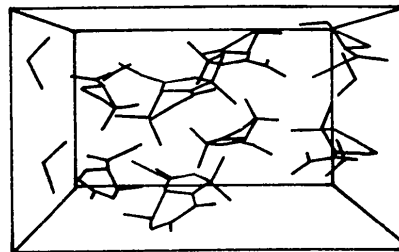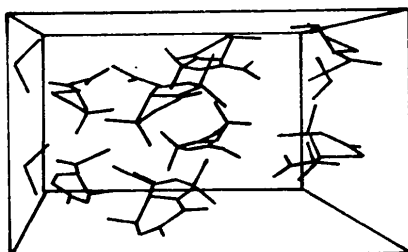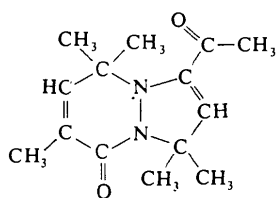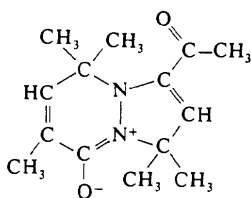
Fig. 6. A stereo view of the unit-cell content. Axial directions are $b\uparrow$, $c \rightarrow$ and a out from the plane of the paper.

Discussion

The molecule found is illustrated in Fig. 1, which shows the relative positions and thermal ellipsoids of the atoms. Figs. 2 and 3 give the bond lengths and bond angles within the molecule, together with estimated standard deviations. Fig. 4 shows its stereochemical form. The five-membered ring observed is nearly planar, the six-membered ring definitely folded; the short C(3)—C(4) and C(7)—C(8) bond lengths of 1·333 and 1·332 Å mark the positions of the double bonds required for the formulation of structure IV (7-acetyl-3,5,5,9,9-pentamethyl-1,6-diazabicyclo[4.3.0]nona-3,7-dien-2-one). As might be anticipated from the ring substituents, the two N atoms are stereochemically different. The bond between them (1·455 Å) corresponds reasonably to the distance expected for a single bond. Around N(6) the angles are approximately tetrahedral, as in a tertiary amine, and the distances C(5)—N(6) (1·494) and C(7)—N(6) (1·422 Å) are nearer to single than double bonds, though the latter is a little short. Around N(1), on the other hand, the coordination is nearly planar, as in a substituted amide. The distance C(2)—N(1) (1·348) is shortened and C(2)—O(18) (1·240 Å) lengthened [compare C(15)—O(7) (1·215 Å)] as required for the contribution of structures such as (V) to the state of the molecule as a whole.

No unusually short intermolecular distances were found in the structure. Stereoscopic views of the packing of the molecules of $C_{14}H_{20}N_2O_2$ down [010] and [100] are shown in Figs. 5 and 6.

(IV)   (V)

References

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