

P (Corosine, Crasnier, Labarre, Labarre & Leibovici, 1973) with the following values for the torsion angles:  $C(2)-C(1)-C(10)-H(C10) = 180(1)^\circ$ ;  $C(2)-C(1)-C(11)-H(C11) = 177(1)^\circ$ ;  $C(2)-C(1)-C(12)-H(C12) = -177(1)^\circ$ ; where  $180$  and  $-180^\circ$  were predicted in the calculations.

Likewise, the carbonyl group  $C(2)-O(9)$  eclipses the bond  $C(1)-C(12)$ , which corresponds well with the conformation noted (LEM, 60) in the theoretical study and leads to a very short  $C(12)-O(9)$  distance of  $2.692(6) \text{ \AA}$ .

In addition, the carboxylic acid group is in the predicted position, with the same orientation of the hydroxyl  $O(7)-H(O7)$ , defined by the torsion angle  $C(4)-C(6)-O(7)-H(O7)$ ; the crystallographic study gives an angle of  $176(1)^\circ$  where a value of  $180^\circ$  was determined by CNDO/2.

However, a new CNDO/2 calculation performed with the crystallographic data led to an energy (about  $21 \text{ kJ mol}^{-1}$ ) greater than that found from the standard geometry. This may be explained by the fact that in the solid state the molecule exists in the dimer form and the geometrical constraints then observed are not taken into account in a quantum calculation of a molecule described by a regular 'standard' geometry.

The similarity of the conformations found in the solid state and for the free molecule suggests that the general conformation of trans-2-pivaloylcyclopropanecarboxylic acid will remain unchanged in solution and therefore that its activity could be explained from this structure determined by X-ray diffraction.

The trans configuration obtained for this acid is the same as that assigned by NMR to the corresponding alcohol, which indicates that the configuration is indeed retained during the reaction shown in Fig. 1.

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## Hydrogen Bonds in a Dimer of Dimethyl 5-Methyl-2-phenyl-3,4-pyrazolidinedicarboxylate

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**Abstract.**  $C_{14}H_{18}N_2O_4$ , monoclinic,  $P2_1/c$ ,  $a = 10.03(1)$ ,  $b = 14.46(2)$ ,  $c = 20.60(1) \text{ \AA}$ ,  $\beta = 100.24(8)^\circ$ ,  $Z = 8$ ,  $M_r = 278.3$ ,  $D_c = 1.26 \text{ Mg m}^{-3}$ ,  $\mu(\text{Mo } K\alpha) = 0.10 \text{ mm}^{-1}$ . There are two crystallographically independent molecules in the asymmetric

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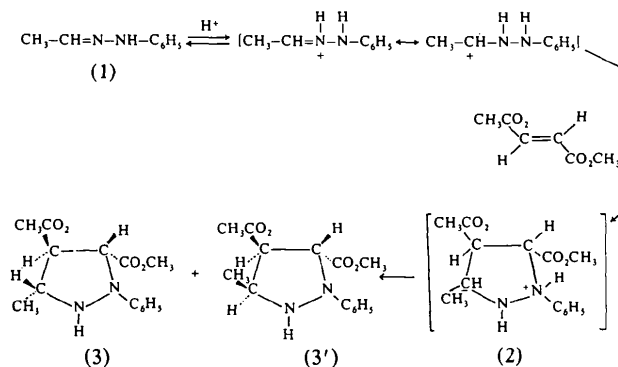
unit. The structure was solved with *MULTAN*. Full-matrix least-squares refinement converged to  $R = 0.054$  for 2041 observed reflexions. The most interesting feature in the structure is the existence of several hydrogen bonds between the two molecules of the

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asymmetric unit. These molecules exist as hydrogen-bonded dimers in the crystalline state, as illustrated by the infrared spectra.

**Introduction.** The addition reaction, in acidic media, of the acetaldehyde hydrazone (1) with fumaric acid dimethyl ester leads to the compound (2), the hydrolysis of which gives a mixture of two epimeric pyrazolidines (3) and (3') (Le Fevre, 1978; Le Fevre, Sinbandhit & Hamelin, 1979).

The same result is obtained in neutral conditions with fumaric acid dimethyl ester and the hydrazone (1) (Le Fevre, 1978; Le Fevre & Hamelin, 1980).



These two types of reaction lead to the synthesis of various pyrazolidines but, in each case, there are always two epimers (about 60%/40%) which may be isolated in crystalline form. It has not been possible to determine unambiguously the structure of each epimer;

studies with  $^1\text{H}$  and  $^{13}\text{C}$  NMR techniques did not completely solve the relative stereochemistry of C(1), C(2) and C(3). Furthermore, this stereochemistry is necessary for a good understanding of the mechanism of these types of polar cycloadditions. The knowledge of the X-ray structure of the compound (3) was necessary (and sufficient), the structure of all other derivatives being deduced.

Crystals were obtained by slow evaporation of a saturated solution in anhydrous ethanol. The approximate dimensions of the sample used in the X-ray analysis were  $0.3 \times 0.2 \times 0.2$  mm. Cell parameters were refined by a least-squares fitting from 14 reflexions. Diffraction intensities were measured with an Enraf-Nonius CAD-4 automatic diffractometer using Zr-filtered  $\text{Mo K}\alpha$  radiation. A  $\theta/2\theta$  scan was used with a scan range of  $1^\circ$ . 3314 independent reflexions were measured out to  $2\theta = 60^\circ$  but only 2041 reflexions were considered according to the criterion:  $|F_o| > 6\sigma(|F_o|)$  and were used for the structure determination. The intensities were corrected for Lorentz and polarization effects but no absorption correction was applied.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) using 340 reflexions with  $E > 1.30$  and 2000 phase relationships. The  $E$  map computed with the set of best consistency (COMBINED FOM = 2.9995) revealed very clearly the positions of all the 40 heavy atoms of the two independent molecules.

Full-matrix least-squares refinement with a  $1/\sigma^2$  weighting scheme was carried out with a modified

Table 1. Final atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters for non-H atoms with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j \text{ (Willis \& Pryor, 1975).}$$

	Molecule A				Molecule B			
	x	y	z	$B_{\text{eq}}$ ( $\text{\AA}^2$ )	x	y	z	$B_{\text{eq}}$ ( $\text{\AA}^2$ )
C(1)	1775 (4)	5255 (3)	842 (2)	2.19 (3)	3410 (4)	5627 (3)	3268 (2)	1.87 (3)
C(2)	2085 (4)	6296 (3)	830 (2)	2.36 (4)	2457 (4)	4870 (3)	3439 (2)	2.13 (3)
C(3)	3652 (4)	6286 (3)	869 (2)	2.75 (4)	3175 (4)	3982 (3)	3267 (2)	2.46 (4)
C(4)	4365 (5)	7179 (3)	1134 (2)	3.93 (5)	2213 (4)	3150 (3)	3111 (2)	3.56 (5)
C(5)	684 (4)	5066 (3)	1255 (2)	2.69 (4)	2604 (4)	6446 (3)	2924 (2)	2.55 (4)
C(6)	-1613 (5)	5405 (3)	1295 (2)	4.62 (5)	1095 (5)	7642 (3)	3084 (2)	4.36 (5)
C(7)	1372 (4)	6763 (3)	210 (2)	2.66 (4)	2221 (5)	4845 (3)	4139 (2)	2.73 (4)
C(8)	478 (5)	8184 (3)	-231 (2)	3.86 (5)	3187 (5)	5108 (3)	5270 (2)	4.23 (5)
C(9)	3510 (5)	4022 (3)	851 (2)	2.53 (4)	5649 (4)	5312 (3)	2981 (2)	2.51 (4)
C(10)	4888 (5)	3783 (3)	969 (2)	3.52 (5)	6554 (5)	4584 (3)	2958 (2)	3.35 (5)
C(11)	5289 (5)	2967 (4)	699 (3)	4.14 (5)	7943 (5)	4767 (4)	3123 (2)	4.32 (5)
C(12)	4394 (6)	2399 (3)	321 (2)	4.22 (5)	8426 (5)	5648 (4)	3277 (2)	4.25 (5)
C(13)	3057 (5)	2624 (3)	204 (2)	3.64 (5)	7528 (5)	6360 (3)	3283 (2)	3.63 (5)
C(14)	2586 (4)	3425 (3)	468 (2)	3.08 (4)	6142 (5)	6197 (3)	3135 (2)	2.76 (4)
N(1)	3075 (3)	4816 (2)	1144 (2)	2.56 (4)	4221 (3)	5179 (2)	2823 (1)	2.10 (3)
N(2)	4098 (3)	5518 (2)	1319 (2)	2.90 (4)	3789 (3)	4237 (2)	2704 (2)	2.47 (4)
O(1)	784 (3)	4593 (2)	1738 (1)	3.96 (5)	2678 (3)	6733 (2)	2398 (1)	5.23 (6)
O(2)	-440 (3)	5526 (2)	981 (1)	3.25 (5)	1874 (3)	6824 (2)	3327 (1)	3.10 (4)
O(3)	1175 (3)	6432 (2)	-330 (1)	3.57 (5)	1230 (3)	4546 (2)	4300 (1)	4.69 (5)
O(4)	1070 (3)	7636 (2)	338 (1)	3.28 (5)	3279 (3)	5167 (2)	4575 (1)	3.37 (5)

Table 2. Final atomic coordinates ( $\times 10^3$ ) for H atoms with *e.s.d.*'s in parentheses

	Molecule A			Molecule B		
	x	y	z	x	y	z
H(N2)	388 (3)	575 (2)	173 (2)	313 (3)	427 (2)	237 (2)
H(C1)	145 (3)	501 (2)	35 (2)	399 (3)	589 (2)	369 (2)
H(C2)	182 (3)	663 (2)	123 (2)	161 (3)	491 (2)	317 (2)
H(C3)	391 (3)	615 (2)	39 (2)	387 (3)	383 (2)	366 (2)
H1(C4)	533 (4)	714 (2)	108 (2)	184 (3)	303 (2)	353 (2)
H2(C4)	401 (3)	774 (2)	90 (2)	164 (3)	329 (3)	276 (2)
H3(C4)	418 (3)	727 (2)	156 (3)	274 (4)	264 (2)	297 (2)
H1(C6)	-184 (3)	479 (2)	134 (2)	46 (3)	745 (2)	271 (2)
H2(C6)	-144 (3)	574 (2)	174 (2)	69 (3)	786 (2)	341 (2)
H3(C6)	-231 (4)	581 (2)	104 (2)	183 (3)	810 (2)	295 (2)
H1(C8)	-16 (4)	787 (2)	-51 (2)	231 (4)	533 (2)	533 (2)
H2(C8)	28 (3)	870 (2)	-3 (2)	361 (4)	559 (2)	547 (2)
H3(C8)	118 (3)	828 (2)	-55 (2)	301 (3)	451 (2)	547 (2)
H(C10)	543 (3)	418 (2)	127 (2)	616 (3)	395 (2)	285 (2)
H(C11)	621 (3)	286 (2)	78 (2)	854 (3)	425 (2)	311 (2)
H(C12)	470 (3)	179 (2)	11 (2)	942 (3)	580 (2)	341 (2)
H(C13)	234 (3)	223 (2)	-4 (2)	782 (3)	699 (2)	339 (2)
H(C14)	166 (3)	356 (2)	36 (2)	557 (3)	671 (2)	313 (2)

version of *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was  $\sum w(|F_o| - |F_c|)^2$ , where  $w$  was obtained from the counting statistics for the observed reflexions.\* Further refinement cycles were carried out using anisotropic temperature factors. A difference Fourier synthesis revealed all the H atoms. Their coordinates were refined but their isotropic thermal parameters ( $4.0 \text{ \AA}^2$ ) were kept fixed during the calculations. The values of the final residuals  $R$  ( $= \sum |F_o| - |F_c| / \sum |F_o|$ ) and  $R_w$  [ $= (\sum w|F_o| - |F_c|)^2 / \sum w|F_o|^2$ ]<sup>1/2</sup> are 0.054 and 0.033 respectively. The final atomic coordinates are given in Table 1 for the heavy atoms and in Table 2 for the H atoms.

**Discussion.** The bond distances and angles for the two molecules are shown in Fig. 1(a,b) with the atom labelling. *ORTEP* drawings (Johnson, 1965) of the two molecules are presented in Fig. 2(a,b). The bond lengths and angles agree with normal ranges. Differences between corresponding bond distances in molecules *A* and *B* are not statistically significant.

The five-membered rings of the two molecules have a satisfactory geometry and their bond distances and angles are very similar. In the two rings, the four heavy atoms C(1), C(2), N(1) and N(2) are planar within  $0.007 \text{ \AA}$  for molecule *A* and  $0.011 \text{ \AA}$  for molecule *B*, the remaining atom C(3) deviating by  $0.592$  and  $0.533 \text{ \AA}$  respectively. Furthermore, in the two cases, the planes defined by atoms C(2), C(3) and N(2) have

\* Lists of structure factors and anisotropic thermal parameters for non-H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36546 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

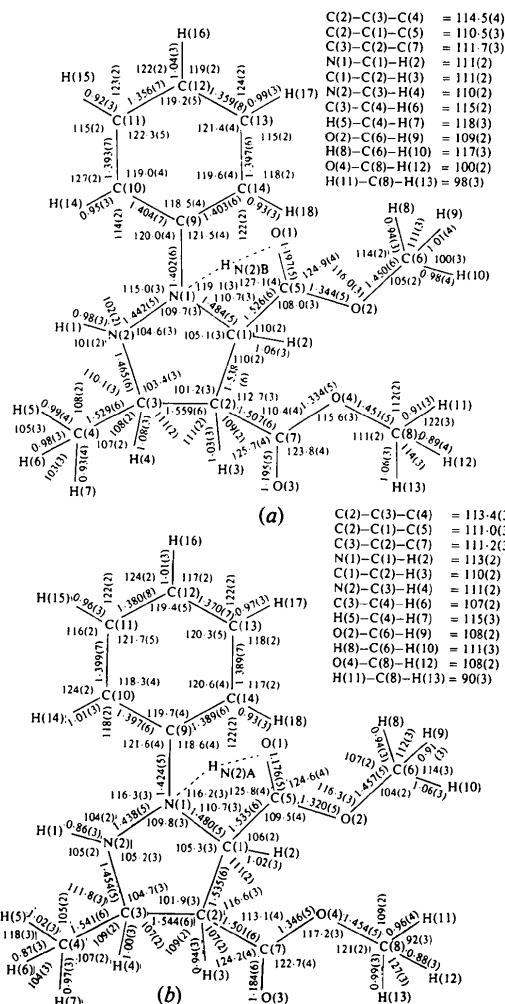


Fig. 1. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in (a) molecule *A* and (b) molecule *B*.

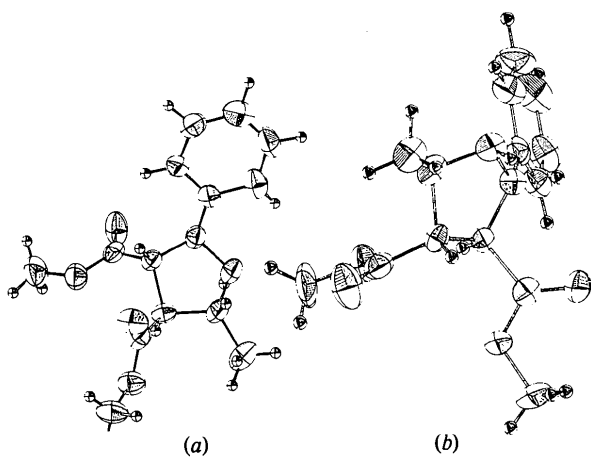


Fig. 2. ORTEP drawing of (a) molecule A and (b) molecule B.

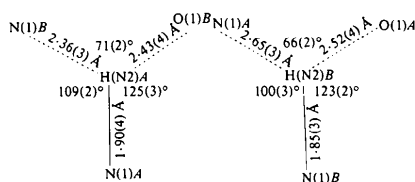


Fig. 3. Hydrogen bonding of H(N2)A and H(N2)B.

very comparable angles with the least-squares planes defined by C(1), C(2), N(1) and N(2) ( $39.2^\circ$  for molecule A and  $35.7^\circ$  for molecule B).

$^1\text{H}$  NMR spectra show a doublet at 1.38 p.p.m. for compound (3), and a doublet at 0.96 p.p.m. for epimer (3') for the methyl group.

The X-ray analysis shows unambiguously that in compound (3), the methyl group is in the *trans* position with respect to the methoxycarbonyl group. Consequently in compound (3') there is a *cis* relationship

between the methoxycarbonyl group and the vicinal methyl group which appears to be shielded at 0.96 p.p.m. This result may be used as a criterion for the stereochemistry of some other analogous pyrazolidines where a methyl group in a *cis* position with respect to a methoxycarbonyl group is shielded.

Finally, we have considered the intramolecular and intermolecular contacts. This study shows that there are two symmetrical groups of hydrogen bridges between the two molecules in the asymmetric unit. The interactions, starting from atoms H(N2)A and H(N2)B respectively, are shown in Fig. 3 and Fig. 1(a,b). The similarity of the corresponding distances and angles can be noted. This may confirm the connexion of the two molecules in the asymmetric unit to form a hydrogen-bonded dimer in the crystalline state. The infrared spectroscopic data in the solid state (Le Fevre & Hamelin, 1980) also confirm this result.

We thank Dr Le Fevre and Professor Hamelin who suggested this study.

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## Structure of 14-Methyl-7-phenylacenaphtho[1,2-*k*]fluoranthene

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**Abstract.**  $\text{C}_{33}\text{H}_{20}$ ,  $M_r = 416.5$ , triclinic,  $P\bar{1}$ ,  $a = 12.184$  (7),  $b = 12.507$  (6),  $c = 8.542$  (3) Å,  $\alpha = 97.64$  (4),  $\beta = 104.45$  (4),  $\gamma = 116.19$  (3)°,  $V = 1085.86$  Å<sup>3</sup>,  $D_x = 1.274$ ,  $D_m = 1.26$  (3) Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 0.077$  mm<sup>-1</sup>,  $Z = 2$ ,  $\lambda(\text{Mo } K\alpha) =$

0.71069 Å,  $F(000) = 436$ . The structure was determined by direct methods. Final  $R = 0.051$  for 2467 observed diffractometer data. The fluoranthene moiety is slightly non-planar; the phenyl ring is almost perpendicular to it and is essentially planar with normal