(Johnson, 1976) view of the molecule perpendicular to the A ring. Fig. 2 shows a projection of the atomic arrangement along the a axis.

Although the structure formulated in Fig. 1 possesses the (S,S)-configuration, the X-ray structure involved a racemate (Fig. 2). The $(\pm)$-isomer is configurationally stable at working temperatures; the *meso* form is not obtained in the synthesis.

The dihedral angle between the benzene rings in the biphenyl moiety is 66·5 (7)°. The methoxy groups occupy a down–up–down–up position, with the methyls diverging from the centre of the cavity. The four methoxy oxygens are at the corners of a tetrahedron, the distances being respectively $O(1)\cdots O(2)$ 3·078 (5), $O(1)\cdots O(2)$ 4·195 (5) Å, $O(1)\cdots O(1')$ 4·255 (9) Å. This arrangement should enhance the hydrophilicity of the cavity.

The imino groups adopt an *anti* conformation as shown in Fig. 1 with the dihedral angle $C(4)$–$C(3)$–$N(2)$–$C(2)$ 176·9 (4)°.

The shape of the cavity may find some use in designing hosts for chiral recognition studies.

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Structures of Eight 2-Dialkylamino-6H-1,3-oxazin-6-ones

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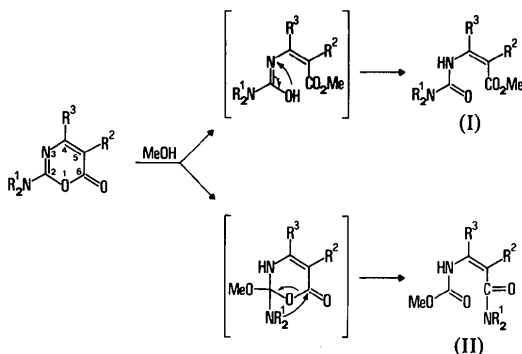
Abstract. (1): 2-Dimethylamino-6-oxo-4-phenyl-6H-1,3-oxazine-5-carbonitrile–0.5 dioxane solvate, $C_{13}H_{11}N_3O_2 \cdot \frac{1}{2}C_4H_8O_2$, $M_r = 285 \cdot 3$, monoclinic, $P2_1/n$, $a = 10 \cdot 127$ (3), $b = 7 \cdot 281$ (1), $c = 19 \cdot 928$ (3) Å, $\beta = 98 \cdot 26$ (2)°, $V = 1454 \cdot 1$ (5) Å^3, $Z = 4$, $D_x = 1 \cdot 303$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0 \cdot 87$ cm^{-1}, $F(000) = 600$, room temperature, final $R = 0 \cdot 065$ for 2484 observed reflections. (2): 5-Benzoyl-2-dimethylamino-4-phenyl-6H-1,3-oxazin-6-one, $C_{19}H_{16}N_2O_3$, $M_r = 320 \cdot 3$, triclinic, $P\bar{1}$, $a = 9 \cdot 603$ (1), $b = 11 \cdot 692$ (2), $c = 8 \cdot 512$ (1) Å, $\alpha = 92 \cdot 01$ (1), $\beta = 110 \cdot 76$ (1), $\gamma = 112 \cdot 05$ (1)°, $V = 812 \cdot 6$ (2) Å^3, $Z = 2$, $D_x = 1 \cdot 309$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0 \cdot 84$ cm^{-1}, $F(000) = 336$, room temperature, final $R = 0 \cdot 043$ for 2962 observed reflections. (3): Ethyl 2-dimethylamino-6-oxo-4-phenyl-6H-1,3-oxazine-5-carboxylate, $C_{15}H_{16}N_2O_4$, $M_r = 288 \cdot 3$, monoclinic, $C2/c$, $a = 15 \cdot 909$ (3), $b = 10 \cdot 711$ (2), $c = 17 \cdot 087$ (3) Å, $\beta = 91 \cdot 98$ (1)°, $V = 2909 \cdot 9$ (9) Å^3, $Z = 8$, $D_x = 1 \cdot 316$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0 \cdot 90$ cm^{-1}, $F(000) = 1216$, room temperature, final $R = 0 \cdot 041$ for 1887 observed reflections. (4): Ethyl 2-dimethylamino-6-oxo-5-phenyl-6H-1,3-oxazine-4-carboxylate, $C_{15}H_{16}N_2O_4$, $M_r = 288 \cdot 3$, monoclinic, $P2_1/c$, $a = 7 \cdot 782$ (1), $b = 11 \cdot 086$ (2), $c = 16 \cdot 993$ (4) Å, $\beta = 97 \cdot 68$ (2)°, $V = 1452 \cdot 9$ (5) Å^3, $Z = 4$, $D_x = 1 \cdot 318$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0 \cdot 90$ cm^{-1}, $F(000) = 608$, room temperature, final $R = 0 \cdot 040$ for 2219 observed reflections. (5): 2-Morpholino-5-o-tolyl-6H-1,3-oxazin-6-one, $C_{15}H_{16}N_2O_3$, $M_r = 272 \cdot 3$, monoclinic, $C2/c$, $a = 19 \cdot 321$ (6), $b = 15 \cdot 868$ (3), $c = 9 \cdot 113$ (3) Å, $\beta = 102 \cdot 40$ (3)°, $V = 2729$ (1) Å^3, $Z = 8$, $D_x = 1 \cdot 326$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0 \cdot 87$ cm^{-1}, $F(000) = 1152$, room temperature, final $R = 0 \cdot 044$ for 2154 observed reflections. (6): Ethyl 2-diisopropylamino-6-oxo-6H-1,3-oxazine-5-carboxylate, $C_{13}H_{20}N_2O_4$, $M_r = 268 \cdot 3$, monoclinic, $P2_1/n$, $a = 12 \cdot 128$ (2), $b = 9 \cdot 836$ (1), $c = 12 \cdot 981$ (2) Å, $\beta = 110 \cdot 10$ (1)°, $V = 1454 \cdot 2$ (4) Å^3, $Z = 4$, $D_x = 1 \cdot 225$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0 \cdot 85$ cm^{-1}, $F(000) = 576$, room temperature, final

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$R = 0.055$ for 1993 observed reflections. (7): Ethyl 2-diisopropylamino-6-oxo-4-phenyl-6H-1,3-oxazine-5-carboxylate, $C_{19}H_{24}N_2O_4$, $M_r = 344.4$, triclinic, $P\bar{1}$, $a = 6.022$ (1), $b = 11.316$ (1), $c = 14.057$ (2) Å, $\alpha = 77.94$ (1), $\beta = 80.61$ (1), $\gamma = 85.81$ (1)°, $V = 923.5$ (2) Å^3, $Z = 2$, $D_x = 1.239$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.82$ cm^{-1}, $F(000) = 380$, room temperature, final $R = 0.036$ for 3022 observed reflections. (8): 2-Dimethylamino-5-o-tolyl-6H-1,3-oxazin-6-one, $C_{13}H_{14}N_2O_2$, $M_r = 230.3$, monoclinic, Cc, $a = 8.548$ (4), $b = 21.169$ (5), $c = 7.323$ (3) Å, $\beta = 113.80$ (3)°, $V = 1212.4$ (9) Å^3, $Z = 4$, $D_x = 1.262$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.81$ cm^{-1}, $F(000) = 488$, room temperature, final $R = 0.063$ for 1018 observed reflections; partial disorder in 6H-1,3-oxazin-6-one group. The reactivity of these molecules is greatly influenced by the nature of the substituents at the positions 4 and 5 of the heterocycle. The C(4)=C(5) double bond is lengthened by introduction of a phenyl ring at 4 and of an electron-withdrawing group such as C=O or C≡N at 5; at the same time the angles at N(3), C(4) and C(5) approach 120°. On exchanging the substituents at 4 and 5, the opposite effect is obtained. The correlation between geometry, steric hindrance and reactivity of 2-dialkylamino-6H-1,3-oxazin-6-ones is evidenced.

Introduction. A series of 2-dialkylamino-6H-1,3-oxazin-6-ones was synthetized by Beccalli & Marchesini (1987) *via* a Vilsmeier–Haack reaction on isoxazolin-5-ones. The reactivities of these molecules vary greatly as a function of the substituents at the heterocycle. For example non-catalytic alcoholysis occurs, at least formally, according to the scheme:

This work was planned to understand, if possible, the relationship between structure and reactivity of the 2-dialkylamino-6H-1,3-oxazin-6-ones, a group nearly unknown in the crystallographic literature.

Experimental. Compounds (2), (4) and (7) were recrystallized from ethyl ether, (3) and (8) from ethyl ether and light ether, (5) from ethyl ether and methylene chloride, (1) from dioxane and (6) from light ether.

Crystal sizes (mm): (1) $0.30 \times 0.30 \times 0.35$, (2) $0.35 \times 0.35 \times 0.35$, (3) $0.24 \times 0.20 \times 0.20$, (4) $0.32 \times 0.28 \times 0.24$, (5) $0.32 \times 0.28 \times 0.25$, (6) $0.30 \times 0.15 \times 0.10$, (7) $0.32 \times 0.32 \times 0.30$, (8) $0.40 \times 0.32 \times 0.30$. Nonius CAD-4 diffractometer with graphite monochromator; lattice parameters measured with 25 reflections in the θ range 14–20° from (1) to (7), and 12–14° for (8); θ–2θ data collection; θ range 0.0–26.0° for (8) and 0.0–27.5° for all other compounds; hkl range: (1) 0→13, 0→9, ±25; (2) 0→12, ±15, ±11; (3) 0→20, 0→13, ±22; (4) 0→10, 0→14, ±22; (5) ±25, 0→20, 0→11; (6) 0→15, 0→12, ±16; (7) 0→7, ±14, ±18; (8) 0→10, 0→26, ±8. Three standard reflections for all compounds; no significant variation of the intensities, with the exception of (1); this specimen quickly lost dioxane with decay of intensity. For this reason a crystal of (1) was sealed in a glass capillary. In spite of this, during data collection a decay of about 16% of check reflections intensity was detected; data were consequently corrected. Data of all structures were corrected for Lorentz and polarization factors but not for absorption. Number of collected data and, in parentheses, number of observed data [criterion $I > \sigma(I)$]: (1) 3327 (2484), (2) 3712 (2962), (3) 3341 (1887), (4) 3325 (2219), (5) 3128 (2154), (6) 3330 (1993), (7) 4214 (3022), (8) 1196 (1018). All structures were solved by direct methods using the program *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); some difficulties arose only for (8): the best E map gave for this structure 12 of the 17 heavy atoms. This structure is partially disordered: the tolyl group is ordered, but the 6H-1,3-oxazin-6-one part of the molecule is present in two orientations rotated exactly by 180° around the C(5)–C(11) bond. The situation is such that only the atom O(7) is split in two distinguishable positions, whereas two conformations of the couples O(1),N(3) and C(4),C(6) are superimposed, so that they are not separable (see Fig. 1h). The ratio O(7)/O(7') was refined to 0.62/0.38. The parameters of H atoms of this structure were not refined, with the exception of those bonded to the benzene ring. Calculated coordinates for the H atoms of dioxane in (1) were also introduced and not refined. All other H atoms in structures (1) to (7) were obtained from difference Fourier maps and were refined isotropically. Heavy atoms were always refined with anisotropic thermal parameters. In all cases the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4I_0/[\sigma^2(I_0) + 0.0004I_0^2]$ and I_0 is the intensity on absolute scale. A secondary-extinction parameter g [Larson (1967), equation (3)] was refined for all structures [$g(\times 10^6)$: (1) 21 (2), (2) 15 (2), (3) 1.6 (2), (4) 10 (1), (5) 3.9 (3), (6) 13 (1), (7) 30 (3), (8) 8 (2)]. Final wR were: (1) 0.041, (2) 0.045, (3) 0.038, (4) 0.043, (5) 0.041, (6) 0.043, (7) 0.060, (8) 0.058. Scattering factors were taken from *International Tables for X-ray Crystal-*

lography (1974). Programs used include Enraf–Nonius (1979) *SDP, ORTEP*II (Johnson, 1976), *PARST* (Nardelli, 1983) and various in-house programs for refinement and geometrical analysis running on a Gould 32/97 computer.*

Discussion. Tables 1–8 list final refined coordinates and U_{eq} values for the non-hydrogen atoms. Fig. 1(a)–(h) shows the molecules with the numbering scheme of heavy atoms; in all structures, the corresponding atoms of the 2-amino-6H-1,3-oxazin-6-one nucleus are given similar numbers. Because of the disorder in the heterocycle ring that could mislead in comparison with the other structures, the results for (8) will not be considered in the discussion.

The deviations from the least-squares plane A through the heterocycle are connected with the steric hindrance of the substituents. The total puckering amplitude (Cremer & Pople, 1975), taken as a measure of non-planarity, is: (1) 0·056 (2), (2) 0·091 (2), (3) 0·034 (2), (4) 0·023 (2), (5) 0·012 (2), (6) 0·029 (3), (7) 0·086 (1) Å²; in all cases distortions are in the direction of a boat or twisted conformation. The largest dihedral angles between plane A and plane B through N(8) and the three carbon atoms bonded to it are 10·28 (5)° in (7) and 9·78 (8)° in (2), the others being in the range 1·8–5·13°. The conformation around N(8) is planar [for (3)] or flat pyramidal: in fact, the maximum deviation from plane B is 0·036 (3) Å for N(8) in (3) and lower in all other structures. The small angle between A and B and the planarity of the amino group account for a strong π conjugation between N(8) and the double-bond chain in the heterocycle; this conjugation is evident from the short N(8)—C(2) bond distance; in fact the mean value of this bond length is 1·325 (6) *vs* 1·313 (7) Å for the formally double bond N(8)—C(2) (see Table 9). The least-squares plane C through the phenyl ring bonded to C(5) [in (4) and (5)] or through the C(5)—CO₂ group [in (3), (6) and (7)] or through C(5), C(17), C(19) and O(18) in (2) is noticeably twisted with respect to the plane A; values between 52·59 (6) and 62·26 (5)° are found; the only exception is (6) for which the angle between A and C is only 9·93 (8)°; in the last case, the conformation is probably determined by the attractive intramolecular interaction O(16)···H(4) [2·46 (2) Å], while in all other cases the conformation is influenced by the repulsive contacts between the atoms or the groups bonded to C(4), C(5) and C(6). The values of the dihedral angle between the plane A and the least-squares plane D through the phenyl ring bonded to

Table 1. *Structure* (1): *fractional coordinates and equivalent isotropic temperature factors* (Å²)

For all structures $U_{eq} = (\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j)/6\pi^2$.

	x	y	z	U_{eq}
O(1)	0·3935 (1)	0·1383 (2)	0·39997 (6)	0·0653 (6)
O(7)	0·2370 (2)	0·0544 (3)	0·46010 (7)	0·0866 (7)
N(3)	0·3533 (2)	0·1710 (2)	0·28032 (7)	0·0549 (6)
N(8)	0·5636 (2)	0·1909 (2)	0·34299 (9)	0·0660 (7)
N(18)	−0·0667 (2)	−0·0014 (3)	0·3517 (1)	0·0845 (9)
C(2)	0·4339 (2)	0·1667 (3)	0·33872 (9)	0·0552 (7)
C(4)	0·2218 (2)	0·1398 (3)	0·28232 (9)	0·0503 (6)
C(5)	0·1736 (2)	0·0972 (3)	0·34201 (9)	0·0534 (7)
C(6)	0·2618 (2)	0·0926 (3)	0·4039 (1)	0·0623 (8)
C(9)	0·6507 (3)	0·1936 (5)	0·4093 (1)	0·084 (1)
C(10)	0·6245 (3)	0·2218 (6)	0·2827 (1)	0·091 (1)
C(11)	0·1360 (2)	0·1552 (3)	0·21552 (9)	0·0520 (7)
C(12)	0·1878 (3)	0·1080 (3)	0·1574 (1)	0·0635 (8)
C(13)	0·1090 (3)	0·1201 (4)	0·0944 (1)	0·080 (1)
C(14)	−0·0196 (3)	0·1817 (4)	0·0890 (1)	0·082 (1)
C(15)	−0·0714 (3)	0·2334 (4)	0·1466 (1)	0·079 (1)
C(16)	0·0063 (2)	0·2196 (3)	0·2092 (1)	0·0632 (8)
C(17)	0·0395 (3)	0·0439 (3)	0·34621 (9)	0·0639 (8)
O(19)	0·3683 (2)	−0·0073 (4)	0·0058 (2)	0·169 (1)
C(20)	0·4280 (4)	−0·1265 (8)	−0·0383 (3)	0·207 (3)
C(21)	0·4342 (5)	0·1579 (7)	0·0208 (3)	0·239 (4)

Table 2. *Structure* (2): *fractional coordinates and equivalent isotropic temperature factors* (Å²)

	x	y	z	U_{eq}
O(1)	0·2203 (1)	0·53759 (8)	−0·0495 (1)	0·0445 (4)
O(7)	−0·0397 (1)	0·40233 (9)	−0·1570 (1)	0·0505 (5)
O(18)	−0·0765 (1)	0·1479 (1)	−0·0587 (1)	0·0672 (5)
N(3)	0·4272 (1)	0·5004 (1)	0·1605 (1)	0·0392 (5)
N(8)	0·4721 (1)	0·6917 (1)	0·0769 (2)	0·0491 (6)
C(2)	0·3746 (2)	0·5732 (1)	0·0671 (2)	0·0384 (6)
C(4)	0·3136 (1)	0·3865 (1)	0·1569 (2)	0·0349 (5)
C(5)	0·1484 (2)	0·3464 (1)	0·0585 (2)	0·0358 (5)
C(6)	0·0959 (2)	0·4223 (1)	−0·0565 (2)	0·0372 (5)
C(9)	0·6416 (2)	0·7429 (2)	0·2012 (3)	0·0609 (8)
C(10)	0·4108 (3)	0·7763 (2)	−0·0175 (3)	0·069 (1)
C(11)	0·3828 (2)	0·3092 (1)	0·2664 (2)	0·0371 (5)
C(12)	0·5297 (2)	0·3683 (1)	0·4098 (2)	0·0463 (6)
C(13)	0·5972 (2)	0·2994 (2)	0·5129 (2)	0·0587 (7)
C(14)	0·5206 (2)	0·1698 (2)	0·4757 (2)	0·0635 (8)
C(15)	0·3772 (2)	0·1094 (2)	0·3342 (2)	0·0574 (8)
C(16)	0·3081 (2)	0·1777 (1)	0·2292 (2)	0·0452 (6)
C(17)	0·0149 (2)	0·2310 (1)	0·0661 (2)	0·0403 (5)
C(19)	−0·0059 (2)	0·2238 (1)	0·2315 (2)	0·0390 (5)
C(20)	−0·0830 (2)	0·1074 (2)	0·2672 (2)	0·0611 (8)
C(21)	−0·1073 (2)	0·1002 (2)	0·4179 (3)	0·071 (1)
C(22)	−0·0593 (2)	0·2070 (2)	0·5309 (2)	0·0590 (8)
C(23)	0·0156 (2)	0·3227 (2)	0·4962 (2)	0·0560 (8)
C(24)	0·0445 (2)	0·3311 (1)	0·3476 (2)	0·0455 (6)

C(4) in (1), (2), (3) and (7) or through C(4)—CO₂ in (4) are quite spread out, being: (1) 33·18 (8), (2) 26·66 (5), (3) 51·68 (6), (4) 68·12 (6) and (7) 39·51 (4)°.

Table 10 gives the bond distances of the disordered structure (8) and, for all other compounds, only the values not belonging to the 2-amino-6H-1,3-oxazin-6-one group are reported. Bond distances and bond angles of the 2-amino-6H-1,3-oxazin-6-one group for (1) to (7) are reported in Table 9; in the eighth column of the same table the mean values over the seven structures are given. As can easily be seen, the dispersion of single values around the mean in some cases is due mainly to (1) and (6). An explanation is

Table 3. *Structure* (3): *fractional coordinates and equivalent isotropic temperature factors* (Å^2)

	x	y	z	U_{eq}
O(1)	0·39900 (9)	0·0568 (1)	0·27081 (8)	0·0503 (5)
O(7)	0·3935 (1)	0·0217 (1)	0·39776 (9)	0·0701 (6)
O(18)	0·3110 (1)	0·3537 (1)	0·44113 (8)	0·0610 (6)
O(19)	0·4275 (1)	0·2605 (2)	0·48946 (9)	0·0833 (8)
N(3)	0·3889 (1)	0·2581 (1)	0·21440 (8)	0·0426 (6)
N(8)	0·3963 (1)	0·0778 (2)	0·14100 (9)	0·0533 (6)
C(2)	0·3941 (1)	0·1357 (2)	0·2089 (1)	0·0428 (7)
C(4)	0·3874 (1)	0·3057 (2)	0·2879 (1)	0·0374 (6)
C(5)	0·3882 (1)	0·2336 (2)	0·3548 (1)	0·0415 (7)
C(6)	0·3940 (1)	0·1012 (2)	0·3483 (1)	0·0480 (7)
C(9)	0·4016 (3)	−0·0589 (2)	0·1350 (2)	0·072 (1)
C(10)	0·3897 (3)	0·1496 (3)	0·0686 (2)	0·077 (1)
C(11)	0·3865 (1)	0·4443 (2)	0·2926 (1)	0·0400 (7)
C(12)	0·3280 (2)	0·5131 (2)	0·2488 (1)	0·0521 (8)
C(13)	0·3261 (2)	0·6417 (2)	0·2550 (2)	0·067 (1)
C(14)	0·3836 (2)	0·7015 (2)	0·3046 (2)	0·072 (1)
C(15)	0·4436 (2)	0·6351 (2)	0·3459 (2)	0·066 (1)
C(16)	0·4449 (2)	0·5068 (2)	0·3403 (1)	0·0526 (8)
C(17)	0·3800 (2)	0·2836 (2)	0·4358 (1)	0·0519 (8)
C(20)	0·2973 (2)	0·4114 (3)	0·5173 (2)	0·083 (1)
C(21)	0·3388 (3)	0·5332 (3)	0·5231 (2)	0·107 (2)

Table 4. *Structure* (4): *fractional coordinates and equivalent isotropic temperature factors* (Å^2)

	x	y	z	U_{eq}
O(1)	0·2522 (2)	0·0036 (1)	−0·01267 (6)	0·0517 (4)
O(7)	0·1203 (2)	−0·0637 (1)	0·08573 (7)	0·0626 (5)
O(12)	0·4753 (2)	0·3579 (1)	0·14341 (7)	0·0659 (5)
O(13)	0·2807 (2)	0·4280 (1)	0·04510 (7)	0·0575 (4)
N(3)	0·3668 (2)	0·1994 (1)	−0·01737 (7)	0·0483 (5)
N(8)	0·3722 (2)	0·0622 (1)	−0·11924 (8)	0·0539 (5)
C(2)	0·3308 (2)	0·0927 (2)	−0·04839 (9)	0·0458 (6)
C(4)	0·3138 (2)	0·2185 (1)	0·05488 (9)	0·0426 (5)
C(5)	0·2288 (2)	0·1380 (1)	0·09641 (9)	0·0417 (5)
C(6)	0·1929 (2)	0·0213 (2)	0·06144 (9)	0·0465 (6)
C(9)	0·4594 (3)	0·1503 (2)	−0·1637 (1)	0·0648 (8)
C(10)	0·3129 (3)	−0·0509 (2)	−0·1580 (1)	0·0704 (9)
C(11)	0·3662 (2)	0·3417 (2)	0·08758 (9)	0·0459 (6)
C(14)	0·3209 (3)	0·5528 (2)	0·0695 (1)	0·0627 (8)
C(15)	0·2175 (4)	0·6320 (2)	0·0105 (2)	0·0693 (9)
C(16)	0·1665 (2)	0·1640 (1)	0·17379 (9)	0·0426 (5)
C(17)	0·0645 (3)	0·2645 (2)	0·1831 (1)	0·0577 (7)
C(18)	0·0056 (3)	0·2875 (2)	0·2550 (1)	0·0680 (8)
C(19)	0·0461 (3)	0·2118 (2)	0·3179 (1)	0·0642 (8)
C(20)	0·1469 (3)	0·1121 (2)	0·3101 (1)	0·0598 (7)
C(21)	0·2072 (2)	0·0885 (2)	0·2387 (1)	0·0496 (6)

Table 5. *Structure* (5): *fractional coordinates and equivalent isotropic temperature factors* (Å^2)

	x	y	z	U_{eq}
O(1)	0·09084 (6)	0·18454 (7)	0·2249 (1)	0·0426 (4)
O(7)	0·07550 (8)	0·19093 (8)	0·4578 (1)	0·0614 (5)
O(11)	0·11611 (7)	0·04940 (8)	−0·2337 (1)	0·0569 (5)
N(3)	0·15057 (8)	0·28792 (9)	0·1153 (2)	0·0477 (5)
N(8)	0·10447 (7)	0·16755 (9)	−0·0111 (1)	0·0454 (5)
C(2)	0·11663 (8)	0·2164 (1)	0·1099 (2)	0·0388 (5)
C(4)	0·15857 (9)	0·3304 (1)	0·2473 (2)	0·0450 (6)
C(5)	0·13494 (8)	0·3061 (1)	0·3707 (2)	0·0377 (5)
C(6)	0·09893 (8)	0·2271 (1)	0·3639 (2)	0·0407 (5)
C(9)	0·0639 (1)	0·0888 (1)	−0·0249 (2)	0·0453 (7)
C(10)	0·1022 (1)	0·0222 (1)	−0·0936 (2)	0·0538 (7)
C(12)	0·1603 (1)	0·1216 (1)	−0·2112 (2)	0·0578 (8)
C(13)	0·1255 (1)	0·1942 (1)	−0·1497 (2)	0·0564 (8)
C(14)	0·14980 (8)	0·3545 (1)	0·5142 (2)	0·0394 (5)
C(15)	0·09584 (9)	0·3856 (1)	0·5789 (2)	0·0494 (6)
C(16)	0·1147 (1)	0·4282 (1)	0·7157 (2)	0·0628 (8)
C(17)	0·1844 (1)	0·4403 (1)	0·7856 (2)	0·0634 (9)
C(18)	0·2373 (1)	0·4121 (1)	0·7190 (2)	0·0651 (8)
C(19)	0·2201 (1)	0·3688 (1)	0·5848 (2)	0·0539 (7)
C(20)	0·0190 (1)	0·3743 (2)	0·5055 (4)	0·083 (1)

Table 6. *Structure* (6): *fractional coordinates and equivalent isotropic temperature factors* (Å^2)

	x	y	z	U_{eq}
O(1)	0·7598 (1)	0·0814 (1)	0·5599 (1)	0·0540 (6)
O(7)	0·7920 (1)	−0·1395 (2)	0·5733 (2)	0·0892 (9)
O(16)	1·1586 (1)	−0·0551 (2)	0·6628 (1)	0·0800 (8)
O(17)	1·0285 (1)	−0·2144 (2)	0·6624 (1)	0·0727 (7)
N(3)	0·9078 (1)	0·2464 (2)	0·5939 (2)	0·0589 (7)
N(8)	0·7112 (1)	0·3023 (2)	0·5431 (1)	0·0496 (7)
C(2)	0·7964 (2)	0·2109 (2)	0·5666 (2)	0·0476 (8)
C(4)	0·9843 (2)	0·1427 (3)	0·6181 (2)	0·0581 (9)
C(5)	0·9593 (2)	0·0073 (2)	0·6182 (2)	0·0491 (8)
C(6)	0·8395 (2)	−0·0318 (2)	0·5848 (2)	0·0572 (9)
C(9)	0·5847 (2)	0·2661 (2)	0·5093 (2)	0·0554 (9)
C(10)	0·5422 (3)	0·1953 (4)	0·3993 (3)	0·085 (1)
C(11)	0·5532 (3)	0·1921 (3)	0·5975 (3)	0·078 (1)
C(12)	0·7422 (2)	0·4496 (2)	0·5535 (2)	0·063 (1)
C(13)	0·6856 (3)	0·5256 (3)	0·4475 (3)	0·080 (2)
C(14)	0·7155 (3)	0·5116 (4)	0·6489 (3)	0·088 (2)
C(15)	1·0591 (2)	−0·0884 (2)	0·6497 (2)	0·0555 (9)
C(18)	1·1238 (2)	−0·3136 (3)	0·6976 (3)	0·078 (1)
C(19)	1·0700 (3)	−0·4486 (3)	0·6774 (3)	0·086 (2)

Table 7. *Structure* (7): *fractional coordinates and equivalent isotropic temperature factors* (Å^2)

	x	y	z	U_{eq}
O(1)	−0·1612 (2)	0·12522 (7)	0·35081 (6)	0·0470 (3)
O(7)	−0·2080 (2)	0·26724 (9)	0·44018 (7)	0·0606 (4)
O(16)	0·0904 (2)	0·51107 (8)	0·24011 (8)	0·0685 (4)
O(17)	0·1884 (2)	0·42521 (9)	0·38581 (7)	0·0630 (4)
N(3)	0·0766 (2)	0·14461 (8)	0·19903 (7)	0·0406 (3)
N(8)	−0·1734 (2)	−0·00924 (9)	0·25487 (8)	0·0469 (4)
C(2)	−0·0813 (2)	0·0895 (1)	0·26543 (9)	0·0391 (4)
C(4)	0·1537 (2)	0·2471 (1)	0·21569 (8)	0·0370 (4)
C(5)	0·0646 (2)	0·2990 (1)	0·29486 (8)	0·0391 (4)
C(6)	−0·1048 (2)	0·2378 (1)	0·36795 (9)	0·0424 (4)
C(9)	−0·3297 (2)	−0·0833 (1)	0·3341 (1)	0·0495 (5)
C(10)	−0·2171 (4)	−0·1396 (2)	0·4222 (1)	0·0689 (7)
C(11)	−0·5519 (3)	−0·0180 (2)	0·3594 (2)	0·0709 (7)
C(12)	−0·1176 (3)	−0·0487 (1)	0·1591 (1)	0·0636 (6)
C(13)	−0·0025 (5)	−0·1721 (3)	0·1690 (3)	0·108 (1)
C(14)	−0·3222 (5)	−0·0389 (3)	0·1084 (2)	0·099 (1)
C(15)	0·1145 (2)	0·4232 (1)	0·30256 (9)	0·0438 (4)
C(18)	0·2351 (4)	0·5435 (2)	0·4023 (2)	0·0801 (8)
C(19)	0·4683 (5)	0·5765 (3)	0·3561 (2)	0·109 (1)
C(20)	−0·3478 (2)	0·2969 (1)	0·14240 (9)	0·0390 (4)
C(21)	−0·5274 (2)	0·3438 (1)	0·1709 (1)	0·0465 (5)
C(22)	−0·7107 (2)	0·3858 (1)	0·1015 (1)	0·0562 (6)
C(23)	−0·7155 (3)	0·3813 (1)	0·0046 (1)	0·0588 (5)
C(24)	−0·5390 (3)	0·3349 (1)	−0·0245 (1)	0·0576 (5)
C(25)	−0·3554 (3)	0·2915 (1)	0·0439 (1)	0·0483 (5)

Table 8. *Structure* (8): *fractional coordinates and equivalent isotropic temperature factors* (Å^2)

	x	y	z	U_{eq}
O(1),N(3')	0·0030	0·0491 (2)	0·2949	0·065 (2)
O(7)	0·0483 (9)	0·1502 (2)	0·292 (1)	0·080 (3)
O(7')	0·450 (1)	−0·0038 (5)	0·342 (2)	0·088 (5)
N(3),O(1')	0·2023 (7)	−0·0264 (2)	0·3011 (8)	0·063 (2)
N(8)	−0·0586 (7)	−0·0547 (2)	0·2855 (9)	0·071 (2)
C(2)	0·0512 (8)	−0·0105 (3)	0·2927 (8)	0·063 (2)
C(4),C(6')	0·3174 (8)	0·0209 (2)	0·3192 (8)	0·054 (2)
C(5)	0·2813 (8)	0·0835 (2)	0·3301 (9)	0·053 (2)
C(6),C(4')	0·1146 (8)	0·0991 (2)	0·3079 (9)	0·064 (2)
C(9)	−0·2286 (9)	−0·0399 (3)	0·274 (1)	0·092 (3)
C(10)	−0·0145 (9)	−0·1220 (3)	0·281 (1)	0·088 (3)
C(11)	0·4132 (8)	0·1336 (2)	0·3497 (9)	0·063 (2)
C(12)	0·4596 (9)	0·1767 (2)	0·498 (1)	0·077 (3)
C(13)	0·5919 (9)	0·2218 (3)	0·516 (1)	0·087 (4)
C(14)	0·668 (1)	0·2180 (3)	0·386 (1)	0·095 (4)
C(15)	0·622 (1)	0·1747 (4)	0·236 (1)	0·097 (3)
C(16)	0·4940 (8)	0·1312 (3)	0·213 (1)	0·076 (3)
C(17)	0·387 (1)	0·1779 (3)	0·648 (1)	0·099 (4)

easily found for the angles involving C(6): they are greatly influenced by the interaction of O(7) with the group bonded at C(5); in (6) the small dihedral angle between planes A and C causes a strong repulsive interaction between O(17) and O(7) whose distance is only 2·798 (2) Å; correspondingly, the angle O(7)—C(6)—C(5) is the largest [132·8 (2)°], while O(1)—C(6)—O(7) and O(1)—C(6)—C(5) are the smallest

[113·7 (2) and 113·4 (2)° respectively]; by contrast, the interaction with O(7) of the linear C(5)—C(17)—N(18) in (1) is small, so that O(7)—C(6)—C(5) is reduced to 128·4 (2) and O(1)—C(6)—O(7) and O(1)—C(6)—C(5) are increased to 115·8 (2) and 115·9 (2)° respectively. At the same time, there is a noticeable variation of O(1)—C(6) and O(7)—C(6) bond lengths: 1·388 (2) and 1·215 (3) Å, respectively, in (1) vs
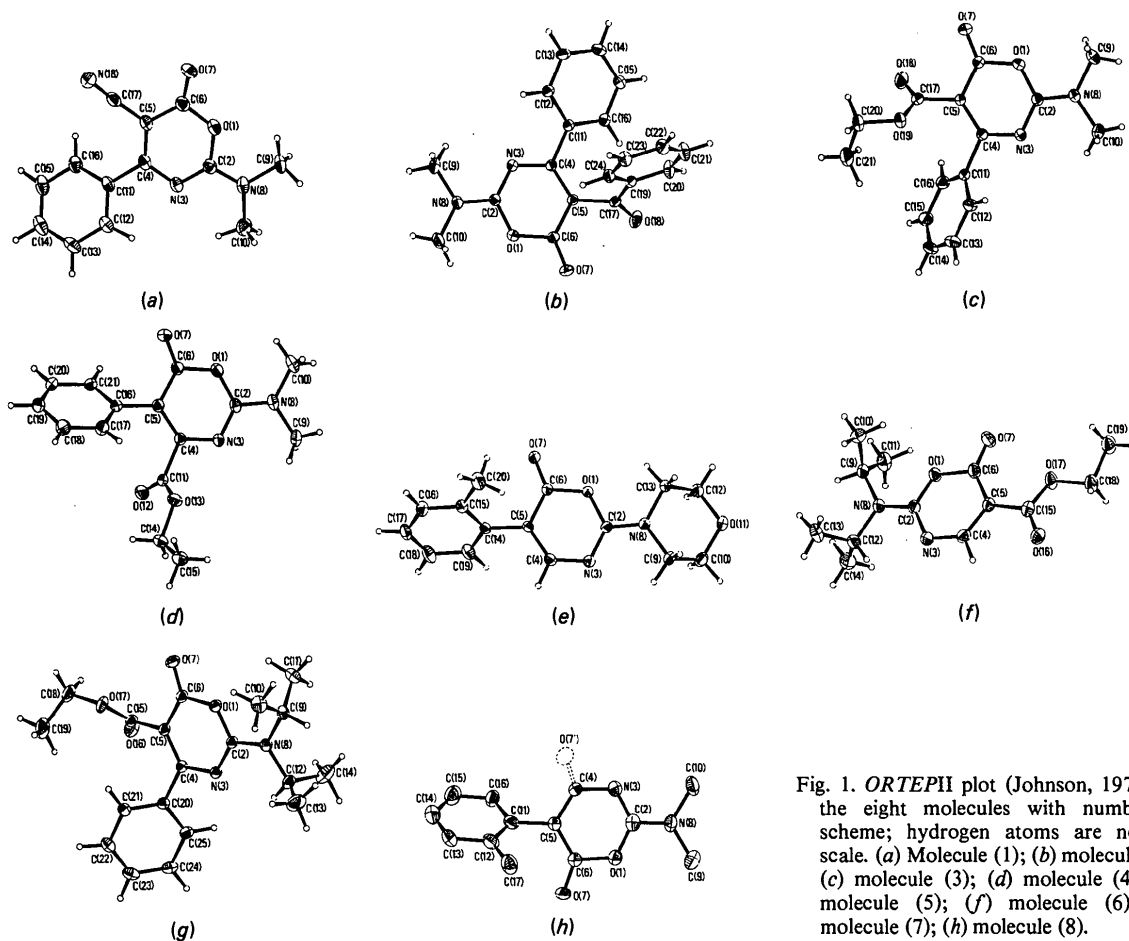

Fig. 1. *ORTEP*II plot (Johnson, 1976) of the eight molecules with numbering scheme; hydrogen atoms are not to scale. (a) Molecule (1); (b) molecule (2); (c) molecule (3); (d) molecule (4); (e) molecule (5); (f) molecule (6); (g) molecule (7); (h) molecule (8).

Table 9. *Bond distances* (Å) *and angles* (°) *of the 2-amino-6H-1,3-oxazin-6-one group*

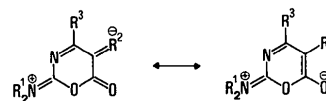|	(1)	(2)	(3)	(4)	(5)	(6)	(7)	Mean
O(1)—C(2)	1·358 (2)	1·349 (2)	1·354 (2)	1·348 (2)	1·352 (2)	1·342 (2)	1·350 (2)	1·350 (5)
O(1)—C(6)	1·388 (2)	1·408 (2)	1·412 (2)	1·412 (2)	1·414 (2)	1·437 (2)	1·419 (2)	1·413 (15)
O(7)—C(6)	1·215 (3)	1·204 (2)	1·200 (2)	1·200 (2)	1·197 (2)	1·191 (3)	1·197 (2)	1·201 (8)
N(3)—C(2)	1·322 (2)	1·303 (2)	1·317 (2)	1·310 (2)	1·306 (2)	1·321 (3)	1·311 (2)	1·313 (7)
N(3)—C(4)	1·357 (3)	1·359 (1)	1·356 (2)	1·363 (2)	1·359 (2)	1·342 (3)	1·358 (2)	1·357 (7)
N(8)—C(2)	1·316 (3)	1·329 (2)	1·317 (2)	1·331 (2)	1·327 (2)	1·329 (2)	1·329 (2)	1·325 (6)
C(4)—C(5)	1·384 (3)	1·382 (2)	1·379 (3)	1·363 (2)	1·357 (3)	1·366 (4)	1·380 (2)	1·373 (11)
C(5)—C(6)	1·416 (3)	1·431 (2)	1·426 (3)	1·436 (2)	1·429 (2)	1·419 (3)	1·428 (2)	1·426 (7)
C(2)—O(1)—C(6)	120·2 (2)	120·2 (1)	121·3 (1)	121·5 (1)	121·9 (1)	122·6 (2)	121·2 (2)	121·3 (9)
C(2)—N(3)—C(4)	117·0 (2)	117·3 (1)	116·3 (2)	115·4 (1)	115·2 (2)	115·0 (2)	117·4 (1)	116·2 (10)
O(1)—C(2)—N(3)	124·6 (2)	124·7 (1)	124·6 (2)	124·5 (1)	124·2 (2)	123·6 (2)	123·7 (1)	124·3 (5)
O(1)—C(2)—N(8)	112·9 (2)	113·2 (1)	113·1 (2)	113·6 (2)	113·4 (2)	114·5 (2)	114·0 (1)	113·5 (6)
N(3)—C(2)—N(8)	122·5 (2)	122·0 (1)	122·4 (2)	121·9 (2)	122·5 (2)	121·9 (2)	122·2 (1)	122·2 (3)
N(3)—C(4)—C(5)	122·1 (2)	122·7 (1)	123·9 (2)	126·2 (1)	126·7 (2)	127·3 (2)	123·3 (1)	124·6 (21)
C(4)—C(5)—C(6)	119·9 (2)	118·8 (1)	119·4 (2)	117·2 (1)	117·4 (2)	117·9 (2)	119·1 (1)	118·5 (10)
O(1)—C(6)—O(7)	115·8 (2)	115·4 (1)	115·1 (2)	115·0 (1)	115·2 (2)	113·7 (2)	115·3 (1)	115·1 (7)
O(1)—C(6)—C(5)	115·9 (2)	115·4 (1)	114·5 (1)	115·2 (1)	114·7 (2)	113·4 (2)	114·4 (1)	114·8 (8)
O(7)—C(6)—C(5)	128·4 (2)	129·3 (1)	130·5 (2)	129·8 (2)	130·2 (2)	132·8 (2)	130·2 (1)	130·2 (14)

1·437 (2) and 1·191 (3) Å in (6). With respect to other geometrical parameters, the seven structures can be divided into two quite homogeneous subsets: the former contains the molecules with a phenyl group bonded at

Table 10. *Bond distances* (Å) *involving heavy atoms and not reported in Table* 9

Compound (1)

O(19)–C(20)	1·430 (7)	O(19)–C(21)	1·387 (6)
N(8)–C(9)	1·480 (3)	N(8)–C(10)	1·445 (4)
N(18)–C(17)	1·145 (4)	C(4)–C(11)	1·486 (2)
C(5)–C(17)	1·426 (4)	C(11)–C(12)	1·382 (3)
C(11)–C(16)	1·383 (3)	C(12)–C(13)	1·390 (3)
C(13)–C(14)	1·367 (4)	C(14)–C(15)	1·381 (4)
C(15)–C(16)	1·380 (3)		

Compound (2)

O(18)–C(17)	1·212 (1)	N(8)–C(9)	1·460 (2)
N(8)–C(10)	1·459 (3)	C(4)–C(11)	1·483 (2)
C(5)–C(17)	1·495 (2)	C(11)–C(12)	1·395 (2)
C(11)–C(16)	1·398 (2)	C(12)–C(13)	1·370 (3)
C(13)–C(14)	1·379 (3)	C(14)–C(15)	1·371 (2)
C(15)–C(16)	1·380 (3)	C(17)–C(19)	1·491 (3)
C(19)–C(20)	1·387 (2)	C(19)–C(24)	1·379 (2)
C(20)–C(21)	1·383 (3)	C(21)–C(22)	1·366 (3)
C(22)–C(23)	1·372 (3)	C(23)–C(24)	1·387 (3)

Compound (3)

O(18)–C(17)	1·336 (3)	O(18)–C(20)	1·464 (4)
O(19)–C(17)	1·194 (3)	N(8)–C(9)	1·470 (3)
N(8)–C(10)	1·457 (4)	C(4)–C(11)	1·487 (3)
C(5)–C(17)	1·494 (2)	C(11)–C(12)	1·386 (3)
C(11)–C(16)	1·387 (3)	C(12)–C(13)	1·382 (3)
C(13)–C(14)	1·383 (4)	C(14)–C(15)	1·367 (4)
C(15)–C(16)	1·378 (3)	C(20)–C(21)	1·464 (5)

Compound (4)

O(12)–C(11)	1·199 (2)	O(13)–C(11)	1·323 (2)
O(13)–C(14)	1·466 (2)	N(8)–C(9)	1·457 (3)
N(8)–C(10)	1·462 (2)	C(4)–C(11)	1·510 (2)
C(5)–C(16)	1·489 (2)	C(14)–C(15)	1·486 (3)
C(16)–C(17)	1·389 (3)	C(16)–C(21)	1·387 (2)
C(17)–C(18)	1·385 (3)	C(18)–C(19)	1·362 (3)
C(19)–C(20)	1·372 (3)	C(20)–C(21)	1·383 (3)

Compound (5)

O(11)–C(10)	1·427 (2)	O(11)–C(12)	1·417 (2)
N(8)–C(9)	1·466 (2)	N(8)–C(13)	1·470 (2)
C(5)–C(14)	1·490 (2)	C(9)–C(10)	1·502 (3)
C(12)–C(13)	1·502 (3)	C(14)–C(15)	1·394 (3)
C(14)–C(19)	1·391 (2)	C(15)–C(16)	1·396 (2)
C(15)–C(20)	1·502 (3)	C(16)–C(17)	1·374 (3)
C(17)–C(18)	1·371 (3)	C(18)–C(19)	1·380 (2)

Compound (6)

O(16)–C(15)	1·205 (3)	O(17)–C(15)	1·320 (3)
O(17)–C(18)	1·461 (3)	N(8)–C(9)	1·487 (3)
N(8)–C(12)	1·491 (3)	C(5)–C(15)	1·476 (3)
C(9)–C(10)	1·511 (4)	C(9)–C(11)	1·512 (5)
C(12)–C(13)	1·508 (4)	C(12)–C(14)	1·512 (5)
C(18)–C(19)	1·463 (4)		

Compound (7)

O(16)–C(15)	1·198 (1)	O(17)–C(15)	1·323 (2)
O(17)–C(18)	1·460 (3)	N(8)–C(9)	1·487 (2)
N(8)–C(12)	1·485 (2)	C(4)–C(20)	1·485 (2)
C(5)–C(15)	1·488 (2)	C(9)–C(10)	1·510 (2)
C(9)–C(11)	1·508 (2)	C(12)–C(13)	1·503 (4)
C(12)–C(14)	1·507 (4)	C(18)–C(19)	1·487 (4)
C(20)–C(21)	1·388 (2)	C(20)–C(25)	1·392 (2)
C(21)–C(22)	1·388 (2)	C(22)–C(23)	1·369 (2)
C(23)–C(24)	1·373 (2)	C(24)–C(25)	1·387 (2)

Compound (8)

O(1)–C(2)	1·329 (8)	O(1)–C(6)	1·402 (7)
O(7)–C(6)	1·205 (7)	O(7')–C(4)	1·20 (1)
N(3)–C(2)	1·31 (1)	N(3)–C(4)	1·372 (8)
N(8)–C(2)	1·311 (9)	N(8)–C(9)	1·46 (1)
N(8)–C(10)	1·478 (8)	C(4)–C(5)	1·370 (6)
C(5)–C(6)	1·41 (1)	C(5)–C(11)	1·512 (8)
C(11)–C(12)	1·350 (8)	C(11)–C(16)	1·43 (1)
C(12)–C(13)	1·44 (1)	C(12)–C(17)	1·46 (1)
C(13)–C(14)	1·35 (1)	C(14)–C(15)	1·36 (1)
C(15)–C(16)	1·39 (1)		

C(4), namely (1), (2), (3) and (7), the latter containing all the others. In the former subset the mean values for the C(4)–C(5) bond length and for the angles C(2)–N(3)–C(4), N(3)–C(4)–C(5) and C(4)–C(5)–C(6) are 1·381 (2) Å, 117·0 (5), 123·0 (8), 119·3 (5)° *vs* 1·362 (5) Å, 115·2 (2), 126·7 (6) and 117·5 (4)° respectively, in the latter.

The thermal or catalytic alcoholysis rate of these compounds increases with the length of the C(4)–C(5) double bond; for example, the thermal reaction with methanol takes about 2 h to complete for (1), (2), (3), (7), 20 h for (6) and about 2 days for (4) and (5) (Beccalli & Marchesini, 1987; Marchesini, 1987). This increasing reaction rate is probably connected with the increasing importance of electronic structures (according to the following scheme) that can favour both nucleophilic and electrophilic attack to the ring.

The ratio between the products (I) and (II) and their formation rate depend mainly on the reaction conditions and on steric effects and less on the ligands at C(4) and C(5). For example, (3) and (4) (with the same substituent exchanged at positions 4 and 5 and giving alcoholysis at very different rates) give about the same ratio of (I)/(II) (about 1:2) in the thermal reaction, whereas in the catalytic one this ratio becomes 2:1 for (3) and tends to ∞ for (4). The slow stage of the reaction to (I) is always the addition of methanol; for the second reaction the shift of the dialkylamino group from C(2) to C(6) is also slow and controls the reaction rate: the rate of this shift is obviously independent of the catalyst. This is probably the reason why the ratio (I)/(II) increases on going from a thermal to a catalytic reaction. The shift of the dialkylamino group from C(2) to C(6) involves the lone pair of N(8) and the p_z orbital of C(6); it is easy to understand that the reaction is strongly affected from steric hindrance due to the substituents at N(8) and at C(5). In fact, (6) and (7), with two cumbersome groups hiding the lone pair of N(8), give only (I), both in thermal and in catalytic alcoholysis. A steric effect due to the group bonded to C(5) is visible in boiling-water hydrolysis; this reaction leads to the acids of (I) and (II) (which decarboxylate immediately); the dihedral angle $\widehat{AC}$ in (6) is only 9·93 (8), *vs* 56·49 (5)° in (7); therefore the interaction between the group bonded at C(5) and the diisopropylamino residue during the shift of the latter from C(2) to C(6) is much stronger for (7) than for (6); in fact, while the latter compound gives the amine derived from decarboxylation of (II), even if at a very slow rate, the former does not react at all under these conditions.

An inspection of the Cambridge Structural Database has shown very few compounds with a 6*H*-

1,3-oxazin-6-one nucleus to be present in the crystallographic literature. Particularly interesting is 2-(m-bromophenyl)-4-acetoxy-6H-1,3-oxazin-6-one (Ammon, Gordon & Ehrenkaufer, 1973). This molecule has the double bonds of the heterocycle ring much more localized than in the compounds which are studied here; in fact, the N(2)—C(3) and C(4)—C(5) bonds are 1·292 (5) and 1·331 (6) Å, respectively.

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Structure of (−)-(6′R)-3′,6′-Epoxyaurapten

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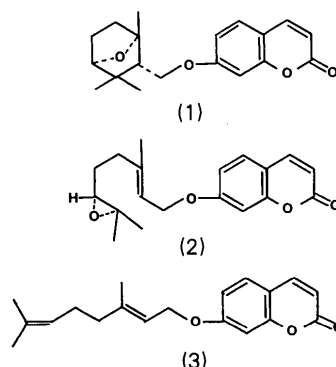AND FRANCIS ROUESSAC AND MOSTAFA AZIZ

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Abstract. 7-[(1,3,3-Trimethyl-7-oxabicyclo[2.2.1]heptan-2-yl)methoxy]-2H-1-benzopyran-2-one, $C_{19}H_{22}O_4$, $M_r = 314·41$, orthorhombic, $P2_12_12_1$, $a = 7·295$ (3), $b = 14·926$ (8), $c = 15·160$ (6) Å, $V = 1651$ (2) Å³, $Z = 4$, $D_x = 1·26$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 0·04$ mm⁻¹, $F(000) = 608$, room temperature. Final $R = 0·046$ for 1625 unique observed reflections, crystal growth from a solution by slow evaporation. The title compound was synthesized with the natural (−) absolute stereochemistry. The cohesion of this structure is due to van der Waals interactions. The characteristics of the lactone ring are consistent with an essentially aliphatic heterocyclic ring. The syn relationship between O2 and C9 postulated by other authors in this series is demonstrated unequivocally.

Introduction. In vegetable life, there are plants in which can be found compounds whose structure seems to stem from the joining of a coumarin and a terpenic heterocyclized chain, corresponding to a 2-alkyl-1,3,3-trimethylbicyclo[2.2.1]heptane, a structure which is rarely found.

(−)-3′,6′-Epoxyaurapten (1) is the simplest representative, found in different species of Asters (Compositae) with (+)-epoxide (2) and the aurapten (3) (Bohlmann, Zdero & Kapteyn, 1968).

(1)

(2)

(3)

After studying various research reports on triterpene biogenesis, we feel that it is reasonable to agree that these three compounds are related, (−)-(1) resulting