is never top-ranking, while it is such in a significant percentage of $P2_12_12_1$ structures for non-centrosymmetric molecules.

The question of what is the most important symmetry operator in an absolute sense is a difficult one, since it is not easy to discern the real effectiveness of each operator in producing close-packed arrays from the effects of the interactions among operators, as dictated by their location in space ('encumbered' operators; Wilson, 1988). Nevertheless, a global analysis of the distribution of organic molecules among space groups, together with the present results, suggest (although no quantitative proof may be given) that the order of importance is $I > S > G > T$. Our results for $P2_1/c$ are, in this respect, exemplary. We note that the importance increases with the number of coordinates whose sign is changed by the operator (3 for I, 2 for S, 1 for G and zero for T).

Of the 177 centrosymmetric molecules in our sample, 67% choose to crystallize in $P2_1/c$, $Z = 2$, 21% in $P\bar{1}$, $Z = 1$, and only 12% in $Pbca$, $Z = 4$; these percentages are quite similar to those found by Scaringe (1990).

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5-Spirocycloalkane Isoxazolines: Structures and Thermal Behaviour

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Abstract

(1): 3-Phenyl-4,5-dihydroisoxazole-5-spirocyclopropane, $C_{11}H_{11}NO$, $M_r = 173.21$, monoclinic, $P2_1/n$, $a = 10.052$ (4), $b = 5.732$ (8), $c = 16.091$ (10) Å, $\beta = 99.41$ (4)°, $V = 915$ (1) Å^3, $Z = 4$, $D_x = 1.26$ g cm^{-3}, $\mu = 0.76$ cm^{-1}, $F(000) = 368$, $T = 298$ K, final $R = 0.094$ for 407 observed reflections [$I > 3\sigma(I)$]. (2): 3-Phenyl-4,5-dihydroisoxazole-5-spirocyclobutane, $C_{12}H_{13}NO$, $M_r = 187.24$, orthorhombic, $P2_12_12_1$, $a = 5.845$ (2), $b = 8.887$ (2), $c = 19.236$ (5) Å, $V = 999.2$ (5) Å^3, $Z = 4$, $D_x = 1.24$ g cm^{-3}, $\mu = 0.74$ cm^{-1}, $F(000) = 400$, $T = 298$ K, final $R = 0.066$ for 679 observed reflections [$I > 3\sigma(I)$]. (3): 3-Phenyl-4,5-dihydroisoxazole-5-spirocyclopentane, $C_{13}H_{15}NO$, $M_r = 201.27$, orthorhombic, $P2_12_12_1$, $a = 8.057$ (10), $b = 11.169$ (5), $c = 12.251$ (9) Å, $V = 1102$ (2) Å^3, $Z = 4$, $D_x = 1.21$ g cm^{-3}, $\mu = 0.71$ cm^{-1}, $F(000) = 432$, $T = 298$ K, final $R = 0.075$ for 502 observed reflections [$I > 3\sigma(I)$]. 5-Spirocyclopropane and 5-spirocyclobutane isoxazolines undergo thermal rearrangement to give mainly 2-phenyl-5,6-dihydropyrid-4-one and 2-phenyl-5,6,7,8-tetrahydro-4*H*-azepin-4-one respectively under rather different experimental conditions. Geometrical parameters of the 5-spirocyclopropane and 5-spirocyclobutane isoxazolines, derived from the X-ray analysis, were used to justify the origin of their different thermal behaviour.

Introduction

Thermal rearrangement of the 5-spirocycloalkane isoxazolines (1) and (2) has recently provided a new route to dihydro-4-pyridone (4) (Guarna, Brandi, De

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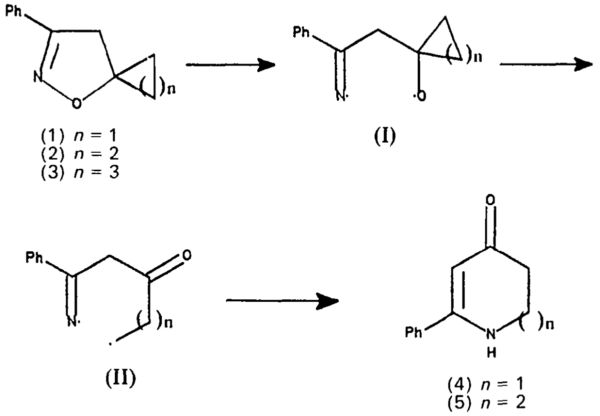
Sarlo, Goti & Pericciuoli, 1988) and tetrahydro-4-azepinone (5) (Goti, Brandi, De Sarlo & Guarna, 1986).



The driving force for the process, shown in the scheme above, results from the strained spirocycloalkane moiety of isoxazolidines (1) and (2) which exhibits a strong tendency to relieve the ring strain present in the system. The presence of an O atom at the spiro centre is expected to lower the activation energy of the process (Trost, 1974).

Therefore, initial homolytic cleavage of the weakest N—O bond of the isoxazolines (1) and (2) is thought to be implicated. This triggers the release of the reactive species (I) which is able to undergo rearrangement *via* the mechanism shown, which involves the diradical (II) (see scheme).

The most effective reaction conditions for the rearrangement of isoxazoline (1) proved to be heating in a solvent, either at reflux or in a sealed tube, between 453 and 473 K for a few hours. None of the starting material is recovered under these conditions, and good yields of the product (4) were obtained (see scheme, $n = 1$). Flash vacuum thermolysis (FVT) at 673 K and 10^{-2} mm Hg was also used successfully.

Analogous rearrangement of the isoxazoline (2) (Goti, Brandi, De Sarlo & Guarna, 1986), leading to the homologous azepin-4-one (5) (see scheme, $n = 2$), requires a considerably higher reaction temperature. The azepinone (5), together with a side product (A. Goti, A. Brandi, F. De Sarlo & A. Guarna, in preparation), was obtained using FVT at 923 K. By contrast, the isoxazoline (2) can be recovered quantitatively after heating for several hours at 473 K in a sealed tube or by FVT at 673 K. The spirocyclopentane isoxazoline (3) is even more stable and was almost completely recovered after FVT at 973 K, in addition to a complex mixture of rearrangement products.

These experimental results demonstrate that the stability of the isoxazoline ring is strongly affected by the size of the ring spiro-fused in the 5 position, although it does not seem to be only related to the difference in strain energy (about 7.5 kJ mol^{-1}) between a cyclopropane and a cyclobutane ring (Engler, Andose & von Schleyer, 1973; von Schleyer, Williams & Blanchard, 1970; Trost, 1986). Since the rate-determining step of the rearrangement should involve cleavage of the N—O isoxazoline bond [formation of intermediate (I), see scheme], the previous experimental observations might infer a close dependence of the structural differentation caused by the size of the spiro-fused ring on the strength of the N—O bond or on other unusual structural parameters in the isoxazolines (1), (2) and (3). The lack of structural analyses on related spiro compounds in the literature has prompted us to resolve the single-crystal X-ray structures of the isoxazolines (1), (2) and (3) in order to elucidate the relationship between structure and reactivity for these compounds.

Experimental

Compounds (1), (2) and (3) were synthesized according to previously reported procedures (Guarna, Brandi, De Sarlo, Goti & Pericciuoli, 1988; Goti, Brandi, De Sarlo & Guarna, 1986; Barbulescu, Grünanger, Langella & Quilico, 1961). Data sets were collected on an Enraf–Nonius CAD-4 diffractometer. 25 reflections were used to determine the cell constants for each compound. Intensity data were corrected for Lorentz and polarization effects. The three structures were solved by the direct-methods routine of *SIR*88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989) and subsequently refined by the full-matrix least-squares technique of *SHELX*76 (Sheldrick, 1976). The function minimized was $\sum w(|F_o| - |F_c|)^2$, with $w = a/\sigma^2(F)$, where a is an adjustable parameter. A summary of the collection and refinement conditions is reported in Table 1. Compound (1): colourless crystals obtained by crystallization from ligroin. During data collection loss of intensity of two standard reflections ($\bar{3}13$, 014) was observed, arising from damage to the crystal due to the low thermal stability of the compound even under these conditions. Intensities were therefore corrected for this effect. Anisotropic thermal parameters were only used for O and N atoms on account of the rather low reflections/parameters ratio. The phenyl group was processed as a regular hexagon. H atoms were introduced in calculated positions with an overall U value of 0.08 Å^2 and were not refined. Compound (2): colourless crystals obtained by crystallization from methanol. No significant variation of intensity was registered for the two monitored standard reflections (410, 150). O and N atoms were refined anisotropically, while isotropic thermal parameters were used for the C atoms. The phenyl group was treated

Table 1. *Crystal and experimental data*

	(1)	(2)	(3)
Crystal dimensions (mm)	0.4 × 0.3 × 0.1	0.6 × 0.5 × 0.2	0.5 × 0.3 × 0.1
Radiation	Mo *Kα* (graphite-monochromated, λ = 0.7107 Å)		
Scan technique	θ–2θ	θ–2θ	θ–2θ
θ range (°)	$5 < 2\theta < 50$	$5 < 2\theta < 50$	$5 < 2\theta < 50$
Scan speed (° min^{-1})	4.0	4.0	4.0
Scan angle (°)	0.8 + 0.35tanθ	0.7 + 0.35tanθ	0.8 + 0.35tanθ
No. of reflections collected	1874	1086	1174
Ref. parameters	52	87	59
wR	0.070	0.048	0.057
S	7.37	7.31	5.06
Max. shift/e.s.d. in last cycle	0.44	0.68	0.52
Final difference Fourier map peaks (e Å^{-3})			
Min.	−0.29	−0.22	−0.27
Max.	0.33	0.26	0.32

as a rigid group and refined as regular hexagon. Compound (3): colourless crystals obtained by crystallization from *n*-hexane. In this case also, no significant variation was found for the standard reflections ($2\bar{1}5$, $25\bar{3}$). The C atoms were refined isotropically, while only the O and N atoms were treated anisotropically on account of the rather low number of observed reflections, probably caused by the particularly small dimensions of the crystal. H atoms were introduced in calculated positions with an overall *U* value of 0.08 Å^2 and were not refined. The phenyl group was refined as a regular hexagon. All calculations were performed on an IBM 2/80 personal computer with the program *SHELX76* using the analytical approximation for the atomic scattering factors and anomalous-dispersion corrections for all atoms (*International Tables for X-ray Crystallography*, 1974, Vol. IV). Tables 2, 3 and 4 list the final atomic coordinates for non-H atoms with their estimated standard deviations.*

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$) *for* $C_{11}H_{11}NO$ (1)

	x	*y*	*z*	$U_{eq/iso}$
O(1)	9749 (8)	2261 (17)	2632 (6)	81 (7)
N(1)	10221 (9)	2706 (18)	1861 (6)	67 (8)
C(1)	11480 (7)	963 (14)	904 (5)	46 (4)
C(2)	12280 (7)	−903 (14)	728 (5)	71 (4)
C(3)	12839 (7)	−907 (14)	−10 (5)	84 (5)
C(4)	12598 (7)	955 (14)	−573 (5)	76 (5)
C(5)	11798 (7)	2822 (14)	−397 (5)	75 (5)
C(6)	11239 (7)	2826 (14)	342 (5)	69 (4)
C(7)	10882 (10)	906 (27)	1662 (7)	46 (4)
C(8)	11027 (11)	−992 (23)	2305 (7)	61 (4)
C(9)	10028 (13)	−146 (27)	2833 (9)	62 (4)
C(10)	8880 (11)	−1551 (22)	3040 (7)	72 (5)
C(11)	9972 (11)	−882 (24)	3709 (7)	76 (4)

Table 3. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$) *for* $C_{12}H_{13}NO$ (2)

	x	*y*	*z*	$U_{eq/iso}$
O(1)	896 (6)	3238 (5)	7800 (2)	75 (3)
N(1)	1723 (8)	2584 (5)	8418 (3)	64 (4)
C(1)	638 (5)	871 (4)	9317 (2)	49 (2)
C(2)	−963 (5)	−162 (4)	9564 (2)	60 (2)
C(3)	−549 (5)	−941 (4)	10181 (2)	73 (2)
C(4)	1467 (5)	−685 (4)	10551 (2)	67 (2)
C(5)	3069 (5)	348 (4)	10304 (2)	69 (2)
C(6)	2654 (5)	1126 (4)	9687 (2)	57 (2)
C(7)	213 (9)	1686 (7)	8666 (3)	47 (2)
C(8)	−1927 (12)	1582 (8)	8233 (3)	54 (2)
C(9)	−1463 (10)	2726 (6)	7662 (3)	52 (2)
C(10)	−1830 (12)	2236 (9)	6910 (3)	63 (2)
C(11)	−4005 (14)	3200 (9)	6911 (4)	71 (2)
C(12)	−3200 (12)	3998 (8)	7565 (4)	64 (2)

Table 4. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$) *for* $C_{13}H_{15}NO$ (3)

	x	*y*	*z*	$U_{eq/iso}$
O(1)	3665 (10)	1538 (6)	8044 (5)	53 (5)
N(1)	3973 (12)	2757 (7)	8274 (7)	52 (7)
C(1)	2933 (8)	4345 (5)	9381 (5)	39 (3)
C(2)	2086 (8)	4647 (5)	10336 (5)	51 (3)
C(3)	2053 (8)	5833 (5)	10691 (5)	63 (4)
C(4)	2868 (8)	6718 (5)	10092 (5)	58 (4)
C(5)	3715 (8)	6417 (5)	9137 (5)	55 (3)
C(6)	3747 (8)	5230 (5)	8782 (5)	46 (3)
C(7)	2946 (14)	3099 (9)	8996 (8)	38 (3)
C(8)	1841 (14)	2133 (9)	9398 (7)	56 (3)
C(9)	2026 (15)	1186 (9)	8525 (8)	48 (3)
C(10)	2217 (14)	−120 (8)	8895 (8)	60 (4)
C(11)	1854 (15)	−817 (10)	7839 (8)	72 (4)
C(12)	1139 (16)	7 (9)	7036 (8)	90 (4)
C(13)	762 (12)	1154 (10)	7614 (8)	58 (4)

Discussion

Selected bond distances and angles of the isoxazoline and cycloalkane rings of (1), (2) and (3) are reported in Table 5. Figs. 1, 2 and 3 show *ORTEP* views (Johnson, 1971) of the crystal structures of (1), (2) and (3) respectively, together with atom labelling. The intermolecular contacts in all derivatives show no unusual features. The overall conformations of the three 5-spirocycloalkane isoxazolines are very similar: the isoxazoline ring and the phenyl group are nearly coplanar, the angles between the two rings being 6.0 (3), 4.3 (2), 19.6 (3)° in (1), (2) and (3) respectively. This planar arrangement is probably due to conjugation involving the phenyl ring and the C—N double bond of the adjacent pentaatomic ring. In fact the bond distances between carbon atoms C(1) and C(7) are shorter (mean value for the three spiroheterocycles, 1.46 Å) than expected for an isolated C—C bond. Furthermore, a weak C—H···N

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54635 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Selected bond distances* (Å) *and angles* (°) *of the isoxazoline and cycloalkane rings for* (1), (2) *and* (3), *with e.s.d.'s in parentheses*

	(1)	(2)	(3)
O(1)—N(1)	1.42 (1)	1.409 (7)	1.41 (1)
O(1)—C(9)	1.44 (2)	1.476 (7)	1.50 (1)
N(1)—C(7)	1.30 (2)	1.282 (8)	1.27 (1)
C(7)—C(1)	1.45 (1)	1.468 (7)	1.47 (1)
C(7)—C(8)	1.49 (2)	1.506 (8)	1.48 (1)
C(8)—C(9)	1.50 (2)	1.521 (8)	1.51 (1)
C(9)—C(10)	1.49 (2)	1.526 (8)	1.54 (1)
C(9)—C(11)	1.48 (2)	–	–
C(9)—C(12)	–	1.531 (9)	–
C(9)—C(13)	–	–	1.51 (1)
C(10)—C(11)	1.46 (1)	1.53 (1)	1.54 (1)
C(11)—C(12)	–	1.52 (1)	1.47 (1)
C(12)—C(13)	–	–	1.49 (1)
N(1)—O(1)—C(9)	106.8 (9)	110.2 (4)	109.2 (7)
O(1)—N(1)—C(7)	109 (1)	109.6 (5)	108.3 (8)
N(1)—C(7)—C(1)	119 (1)	120.5 (5)	120.9 (9)
N(1)—C(7)—C(8)	114 (1)	113.9 (5)	113.8 (9)
C(8)—C(7)—C(1)	126 (1)	125.6 (5)	125.3 (8)
C(7)—C(8)—C(9)	99 (1)	102.1 (5)	102.4 (8)
O(1)—C(9)—C(8)	108 (1)	104.1 (5)	100.5 (9)
O(1)—C(9)—C(10)	116 (1)	112.9 (5)	106.1 (9)
O(1)—C(9)—C(11)	117 (1)	–	–
O(1)—C(9)—C(12)	–	114.5 (5)	–
O(1)—C(9)—C(13)	–	–	108.1 (8)
C(8)—C(9)—C(10)	125 (1)	117.9 (5)	117.8 (8)
C(8)—C(9)—C(11)	126 (1)	–	–
C(8)—C(9)—C(12)	–	117.6 (5)	–
C(8)—C(9)—C(13)	–	–	118.2 (9)
C(10)—C(9)—C(11)	58.8 (8)	–	–
C(10)—C(9)—C(12)	–	90.1 (5)	–
C(10)—C(9)—C(13)	–	–	105.2 (8)
C(9)—C(10)—C(11)	60.3 (8)	87.5 (5)	102.3 (8)
C(10)—C(11)—C(9)	60.9 (8)	–	–
C(10)—C(11)—C(12)	–	90.3 (6)	108.8 (8)
C(9)—C(12)—C(11)	–	87.8 (5)	–
C(11)—C(12)—C(13)	–	–	107.5 (8)
C(9)—C(13)—C(12)	–	–	103.5 (8)

intramolecular hydrogen bond exists between the proton on C(6) of the phenyl group and the nitrogen atom N(1) [contact distances 2.49 (1), 2.499 (7), 2.54 (1) Å for (1), (2) and (3) respectively] which contributes to the stabilization of the planar conformation. In all three derivatives the cycloalkane ring lies in a quasi-perpendicular plane with respect to the isoxazoline ring, the angular values between the mean-squares planes being 90.6 (7), 91.7 (3), 98.4 (3)° for (1), (2) and (3) respectively. The geometrical parameters of the cycloalkane rings are as expected for the unsubstituted molecules; the cyclobutane and cyclopentane rings show as expected (Allinger, Tribble, Miller & Wertz, 1971) significant deviations from planarity, the largest deviations being 0.13 (1) Å for C(11) and 0.24 (1) Å for C(9). The isoxazoline ring is nearly planar in all three compounds, the largest deviation from planarity being observed for the spiro carbon C(9) of the cyclopropane derivative, which is 0.14 (1) Å out of the least-squares plane. The N—O bond, whose cleavage is involved in the rate-determining step (see scheme), has a similar length in all three compounds [1.42 (1), 1.409 (7), 1.41 (1) Å for (1), (2) and (3) respectively]. Therefore the different thermal reactivities of the 5-spirocycloalkane isoxazolines cannot be explained by differences in the strength of this bond. The only significant geometrical difference between the three molecules involves the spiro carbon atom C(9). In particular the angles around this atom, shared by the two spiro-fused rings, differ significantly in the three compounds because of the different stereochemical requirements of the three cycloalkane rings (Table 5). The isoxazoline ring opening, which we believe to be involved in the rate-determining step, directly involves five of the six angles around the C(9) atom. In order to study the effect of the isoxazoline ring opening on these angles we carried out a search of the Cambridge Structural Database (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink, Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979) to discover typical angular values of C, O *gem*-disubstituted cycloalkanes, considering this stereochemical arrangement to be comparable to that obtained after the N—O bond cleavage [see scheme, intermediate (I)]. On account of the scarcity of crystal structures containing O—$C_{cycloalkane}$—C angles, C—$C_{cycloalkane}$—C angles were

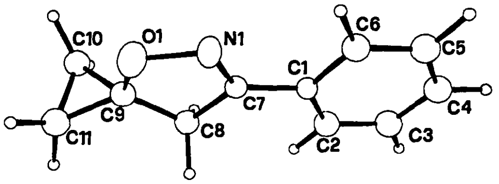


Fig. 1. *ORTEP* view of the compound $C_{11}H_{11}NO$ (1). For convenience a non-conventional atom labelling was used in all the structures.

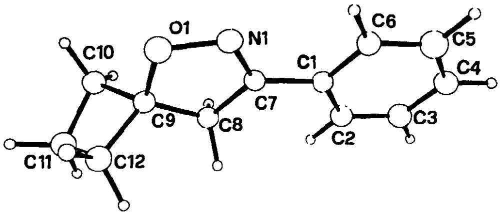


Fig. 2. *ORTEP* view of the compound $C_{12}H_{13}NO$ (2).

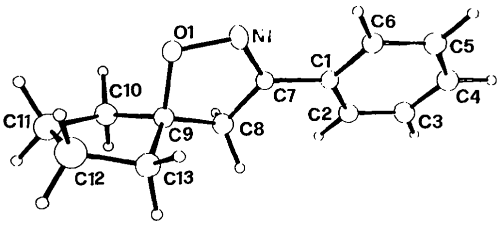
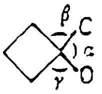
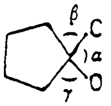


Fig. 3. *ORTEP* view of the compound $C_{13}H_{15}NO$ (3).

Table 6. *Reference angular values* (°) *used to evaluate the bending-energy content of the molecular fragment around the spiro carbon atom* C(9)

Molecular fragment	Angle	
	α	$\beta = \gamma$
	117.9	116.5
	107.0	115.2
	107.8	111.5

also considered. Only three reference structures were found for both cyclopropane and cyclobutane derivatives, whereas four structural determinations were found having the cyclopentane *gem*-disubstituted fragment. All of these structures were then utilized; the maximum standard deviation on the C—C—C angles is about 1.0°. Table 6 lists the mean angular values obtained from these bibliographic data which were used as reference values to calculate the bending-energy content of the five angles involving the C(9) carbon atom in the three derivatives. The bending force constants employed in these calculations were taken from Snyder & Schachtschneider, 1965. The bending energy of the angles around the C(9) atom of the spirocyclopropane derivative is about 20 kJ mol^{-1} higher than the spirocyclobutane, which gives analogous rearrangement products. Therefore, because this result agrees well with experimental evidence, the different stereochemical arrangement of the spiro C(9) atom seems to be a good structural explanation for the differences observed in the FVT reaction of these two derivatives. On the other hand, the behaviour of the cyclopentane derivative, which shows a more complex reaction pathway, cannot be explained on the basis of the different bending-energy content alone (about 8 kJ mol^{-1} less than the cyclopropane derivative).

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