Crystal and Molecular Structure of 3-Chloro-5-phenylisoxazole

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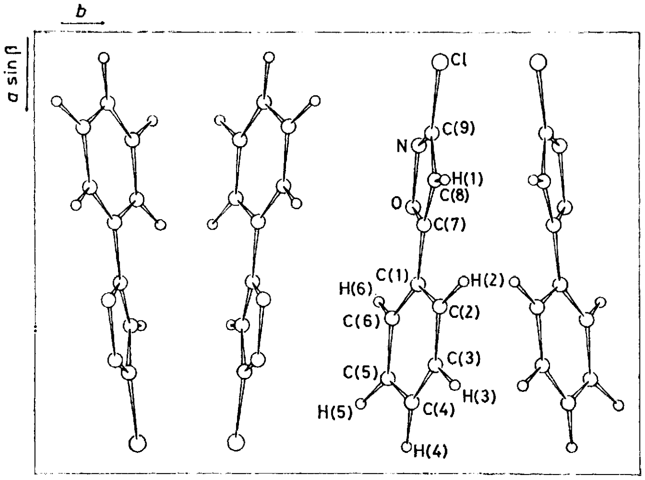
The crystal structure of 3-chloro-5-phenylisoxazole has been determined from three-dimensional *X*-ray data. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions: $a = 10.95(3)$, $b = 14.27(4)$, $c = 5.83(2)$ Å, $\beta = 108.1(5)°$. The structure was refined by block-diagonal least-squares methods to a final *R* of 0.096 for 636 observed reflections. The phenyl and isoxazole rings are twisted by 15°, and this non-coplanarity is discussed in connection with CNDO/II calculations.

THE configuration of molecules in which two aromatic rings are linked by a C–C single bond is reached through a balance between the effects caused by delocalization of π electrons and steric hindrance of atoms in *ortho*-positions: the first factor favours co-planarity and the other orthogonality of the two rings. In the solid state a further factor, which favours the configuration leading to a close molecular packing, must be taken into account. This last effect is well known for biphenyl, where the two rings are twisted by 42° in the vapour phase,[1] but are coplanar in the crystal.[2]

The crystal structures of several phenyl- and bi-isoxazole molecules [3] have shown them to be planar.



Projection of the structure along the *c* axis

This planarity is certainly favoured by the presence of the five-membered rings, which by increasing the value of the external bond angles around the carbon atoms involved in the inter-ring bond, lessen the steric hindrance of the hydrogen atoms in *ortho*-positions.

We have now completed the structural analysis of 3-chloro-5-phenylisoxazole and found that it is the first example of a phenyl- or bi-isoxazole in which the rings are not coplanar in the crystal. A projection of the crystal structure is shown in the Figure. Bond distances and angles (Table 1) are close to those found in analogous compounds; [3] the value of angle O–C(7)–C(1) is lower than that of C(8)–C(7)–C(1), reducing the steric hindrance between H(1) and H(2).

3-Chloro-5-phenylisoxazole, therefore, differs from the compounds previously examined; [3] the least-squares planes, fitted to isoxazole and phenyl rings separately, form an angle of *ca.* 15°. This configuration is very close to that obtained by CNDO/II calculations,[4] which were performed for four conformations, corresponding to values of 0, 10, 20, and 40° for the dihedral angle between the ring planes. The corresponding total energy values (71 964.684 0, 71 964.725 4, 71 964.964 2, and 71 964.496 3 kcal) were fitted to a parabolic function which has a minimum around 18°. The surprising agreement between experimental and theoretical values could be related to the loose crystal packing, as shown by the absence of short intermolecular contacts, by the m.p. (37 °C) and by the low value (0.68) of the packing density *K*, where *K* is defined [5] as ZU_0/U, where *Z* is the number of molecules in the unit cell, *U* is the cell volume, and U_0 the molecular volume calculated from known atomic and intermolecular radii and valence angles. The value of *K* is very close to the lower limit of the range generally found for molecular crystals. In the case of the α- [3a] and β-isomers [3b] of 3-hydroxy-5-phenylisoxazole, which have the same steric requirements as 3-chloro-5-phenylisoxazole but are planar, the values of *K* are 0.75 and 0.73, and are very close to the upper experimental limit. These results, as do those for some biphenyl derivatives, seem to suggest that a planar configuration, if sterically permitted, is assumed in the solid state whenever intermolecular interactions lead to close packing (high *K*): *e.g.* α- and β-3-hydroxy-5-

TABLE 1

Bond distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Distances			
Cl–C(9)	1.70(1)	C(1)–C(2)	1.41(2)
N–C(9)	1.33(1)	C(2)–C(3)	1.39(2)
N–O	1.43(1)	C(3)–C(4)	1.41(2)
O–C(7)	1.37(1)	C(4)–C(5)	1.41(2)
C(7)–C(8)	1.34(2)	C(5)–C(6)	1.41(2)
C(8)–C(9)	1.39(2)	C(6)–C(1)	1.45(2)
C(1)–C(7)	1.45(2)		
(*b*) Angles			
Cl–C(9)–N	117.0(0.9)	C(8)–C(7)–C(1)	132.9(1.0)
Cl–C(9)–C(8)	129.3(0.8)	C(7)–C(1)–C(6)	119.1(0.9)
N–C(9)–C(8)	113.7(1.0)	C(1)–C(2)–C(3)	119.6(1.1)
O–N–C(9)	103.0(1.0)	C(2)–C(1)–C(6)	119.2(1.0)
N–O–C(7)	108.4(0.9)	C(2)–C(3)–C(4)	122.1(1.1)
C(9)–C(8)–C(7)	105.4(1.0)	C(3)–C(4)–C(5)	119.3(1.1)
O–C(7)–C(8)	109.5(1.0)	C(4)–C(5)–C(6)	119.7(1.1)
O–C(7)–C(1)	117.7(0.9)	C(5)–C(6)–C(1)	120.1(1.0)
C(7)–C(1)–C(2)	121.7(1.0)		

phenylisoxazole, biphenyl 0.72,[2] and *p,p'*-dihydroxybiphenyl 0.73.[6] If the interactions are weak (low K) the molecules retain a configuration closer to that of the gas phase: *e.g.* 3-chloro-5-phenylisoxazole 0.68, *p,p'*-dinitrobiphenyl 0.68,[7] *p*-nitrobiphenyl 0.69,[8] and *p,p'*-bitolyl 0.70.[9]

EXPERIMENTAL

The compound was synthesized according to the method of ref. 10. Crystals, m.p. 37—38 °C, suitable for X-ray analysis, were obtained by evaporation of a concentrated hexane solution. Unit cell dimensions were determined from zero-level Weissenberg photographs taken around the b and c axes.

Crystal Data.—C_9H_6ClNO, $M = 179.5$. Monoclinic, $a = 10.95(3)$, $b = 14.27(4)$, $c = 5.83(2)$ Å, $\beta = 108.1(5)°$, $U = 866$ Å^3, $D_m = 1.37 \pm 0.02$, $Z = 4$, $D_c = 1.37$. Cu-K_α radiation, $\lambda = 1.541\,8$ Å; μ(Cu-K_α) = 33.3 cm^{-1}. Space group $P2_1/c$ from systematic absences: $h0l$ for $l = 2n + 1$; $0k0$ for $k = 2n + 1$.

Intensities for $hk0$—3 and $h0$—$7l$ reflections were collected on an integrating Weissenberg camera from two crystals mounted along c and b respectively and determined photometrically with the aid of a microdensitometer. A total of 868 reflections were measured; after correction for Lorentz and polarization factors, they were placed on the same relative scale by a least-squares procedure [11] and reduced to a set of 479 independent reflections. The weakest reflections (157) were visually estimated with the aid of a calibrated scale. The 598 unobserved reflections up to θ 65° were given an F_0 value equal to half the minimum observed. Atomic scattering factors were taken from ref. 12 for chlorine, oxygen, nitrogen, and carbon, and from ref. 13 for hydrogen.

Structure Determination and Refinement.—The structure was solved by direct methods, using the automatic program coded in SHELX 76 for centrosymmetric structures.[14] An E map clearly showed all non-hydrogen atom positions. Three cycles of full-matrix least-squares cycles with isotropic temperature factors and unit weights reduced R to 0.21 for the 479 photometrically observed reflections. At this point all the 636 observed reflections were included in the refinement, which proceeded by block-diagonal least-squares methods, with anisotropic temperature factors; hydrogen atoms were also introduced and held fixed at calculated positions with a B value of 8.5 Å^2; weights were calculated as $1/A + BF_0 + CF_0^2$ with $A = 12.5$, $B = 0.23$, and $C = 0.001\,4$. After six cycles refinement converged at R 0.096. The R value for the 1 234 observed and unobserved reflections was 0.156. Final atomic positional parameters with estimated standard deviations are given in Table 2. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22360 (8 pp., 1 microfiche).*

TABLE 2

Atom co-ordinates, with standard deviations in parentheses

	x	y	z
Cl	703(3)	6 584(3)	3 363(6)
O	3 941(7)	6 116(6)	7 984(12)
N	2 572(10)	6 210(8)	7 241(18)
C(1)	5 713(9)	6 208(7)	6 364(17)
C(2)	6 262(12)	6 575(9)	4 667(17)
C(3)	7 579(12)	6 507(9)	5 095(22)
C(4)	8 398(12)	6 078(9)	7 192(21)
C(5)	7 869(13)	5 704(9)	8 910(21)
C(6)	6 539(11)	5 786(8)	8 548(19)
C(7)	4 351(11)	6 275(8)	6 019(15)
C(8)	3 340(11)	6 469(8)	4 096(18)
C(9)	2 283(10)	6 434(9)	4 919(17)

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, Index issue, 1978.