

characterized by two angles θ_1 ($\langle C_1-X_1...X_2 \rangle \approx 90^\circ$ and θ_2 ($\langle C_2-X_2...X_1 \rangle \approx 180^\circ$ and (b) Type III where $\theta_1 = \theta_2$. When there is a dominant interaction of X with E or Nu, the electrophile-nucleophile pairing is no longer clear-cut, but Type III ($\theta_1 = \theta_2$) interactions persist. A plot of the number of $Br...O$ and $I...O$ interactions as a function of d_{X-O} shows undulations but that of $Cl...O$ does not. It is interesting to point out that both the monovalent halogens X in their $X...X$ interactions and divalent S and Se in their $S...S$ and $Se...Se$ interactions show the "electrophile-nucleophile" pairing and Type III contacts.

*Work supported by a grant from the National Institutes of Health, NCI CA23704.

04.2-3 CONFORMATION AND ABSOLUTE CONFIGURATION OF A KETONE DERIVATIVE OF GALLICIN, A TEN-MEMBERED RING SESQUITERPENE. By M.A. Gomez-Rodriguez, M. Martinez-Ripoll and S. Garcia-Blanco. Dept. Rayos X, Inst. Rocasolano, Serrano 119, Madrid-6, Spain.

The present investigation forms part of a study on the high stereoselectivity of the cyclization processes of sallicin and its derivatives (A.G. Gonzalez et al. J. Chem. Soc. Perkin Trans. 1, 2, 1243, 1978), (A.G. Gonzalez et al. Tetrahedron Letters, 39, 3769, 1979), (A.G. Gonzalez et al. Tetrahedron, 36, 2015, 1980), (A.G. Gonzalez et al. J. Chem. Soc. Perkin Trans. 1, 881, 1981) and its relations with their conformational aspects.

C15 O3 H22, orthorhombic, P212121, $a=26.236(6)$, $b=8.184(1)$, $c=6.573(1)$ Å, $V=1411.4(1)$ Å³, $Z=4$, $D_c=1.18$ g.cm⁻³, $\mu(CuK\alpha)=6.11$ cm⁻¹. $R=0.050$, $wR=0.062$ for 601 observed Friedel pairs.

The conformation of the ten-membered ring corresponds to CCC (J.B. Hendrickson. J. Am. Chem. Soc., 89, 7036, 1967), and is the same found in sallicin and other sesquiterpenolides. The lactone ring is envelope conformed, the C7 atom being at the flap.

The absolute configuration was determined by comparing the most relevant 54 Bijvoet pairs and is the same as the one found for sallicin (A.G. Gonzalez et al. J. Chem. Soc. Perkin Trans 1, 2, 1243, 1978).

The figure shows a perspective drawing of the X-ray model.

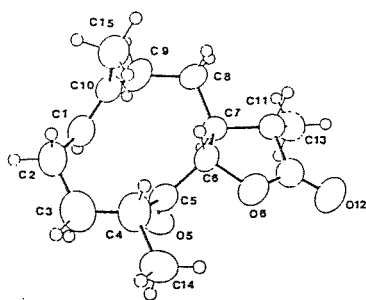


Figure 1.

04.2-4 MOLECULAR STRUCTURE OF o-CHLORO-N-β-CYANOETHYL-ANILIDE. By M. Martinez-Ripoll^a, C. Esteban-Calderón^a, S. Garcia-Blanco^a, L. Canoira^b and J.G. Rodriguez^b. a) Dept. Rayos X, Inst. Rocasolano, Serrano 119, Madrid-6, Spain b) Dept. Q. Ors. Univ. Autónoma, Madrid, Spain

Some N-β-cyanoethyl-o-substituted anilides in solution, show a diastereotopic coupling effect in the H-nmr spectra, due to the methylene protons of the N-β-cyanoethyl chain. An X-ray analysis of the title compound has been carried out to investigate this effect.

C13 H11 N2 O3 Cl, orthorhombic, Pna21, $Z=4$, $a=10.341(3)$, $b=9.820(3)$, $c=12.917(3)$ Å, $V=1312(1)$ Å³, $D_c=1.41$ g.cm⁻³, $\mu(MoK\alpha)=2.93$ cm⁻¹. $R=0.037$, $wR=0.034$ for 1070 observed reflexions.

Fig. 1 shows the Newmann projections of the chain in both a) solution and b) solid state. Fig. 2 represents the molecular structure. The diastereotopic effect of the methylene protons of the chain, occurring in solution, can be improved with the results in solid state: 1) a rigid anchorage of H91 to O1 prevents free rotation of the chain, 2) a dipolar stabilization effect of the gauche π conformation occurs between dipole moments of $-C11=N2$ and $-N1-C9$. This fact leads $C11=N2$ close to $N1-C9$, but only up to the gauche π conformation, because the steric hindrance would prevent the eclipsed conformation, 3) the o-substitution obliges to a rigid positionment of the $-C\equiv N$ function, which cannot rotate closer to the o-group. Rotation in opposite sense is prevented by the dipole charge enhancement mentioned above.

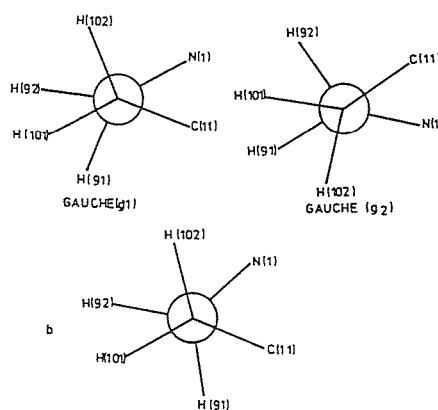


Fig. 1

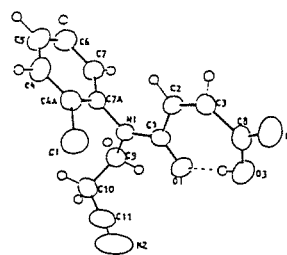


Fig. 2