04.1–16 CRYSTAL STRUCTURE RELATIONSHIPS BETWEEN CYCLO OCTADIENE COMPLEXES OF Pt(II). By F. Mz. Musitu. Dpto. Q. Inorgánica. Colegio Universitario de Alava (UPV). VITORIA and S. Garcia-Blanco. Dpto. Rayos-X, Instituto Rocasolano, CSIC, Serrano 119, MADRID-6. SPAIN.

The crystal structures of $C_8H_{12}PtX_2$ complexes ( where X = Cl, Br, I and SCN ) have been determined by X-ray diffraction.

The crystallografic date are as follow:

| Formulae | $C_8H_{12}PtCl_2$ | $C_8H_{12}PtBr_2$ | $C_8H_{12}PtI_2$ | $C_8H_{12}Pt(SCN)_2$ |
|---|---|---|---|---|
| S. Group | $P2_12_12_1$ | $P2_12_12_1$ | P2/n | $Pna2_1$ |
| a (Å) | 12.3109(10) | 12.4636(20) | 12.9384(5) | 16.8764(26) |
| b | 10.9748(10) | 11.1762(20) | 10.8926(3) | 9.0921(8) |
| c | 6.9220(5) | 7.0747(9) | 8.2958(3) | 7.5982(7) |
| β° | 90 | 90 | 106.90(3) | 90 |

These complexes are compared against those found in the bibliografy of formulae $C_8H_{12}MXY$ (where M = Pt, Pd and Rh). This comparison is made in terms of : a) metal coordination and b) bond and intraanular distances, bond angles and torsion angles, with respect to that of free cyclooctadiene ring.

04.2–1 DEFORMATION OF π-ELECTRON SYSTEMS. By W.H. Watson. Department of Chemistry, Texas Christian University, Fort Worth, Texas USA

The stereoselectivity and accelerated rates of reaction of norbornene and related systems has been shown to be associated with a deformation of the π-electron system. The nominally $sp^2$ hybridized carbon atoms are pyramidalized, which results in the π-system deviating from planarity by bending hinge-like along the C-C bond. In syn-sesquinorbornene and its derivatives the driving force for the pyramidalization has been attributed to ground state torsional effects, antihyperconjugative interactions between π and "cyclopentane ribbon" orbitals and to antihyperconjugative effects between the π-system and specific σ bonds. It has been impossible to experimentally distinguish between these effects.

In general, anti-sesquinorbornene is expected to be planar because the above effects are cancelled due to symmetry. However, if half of the anti-sesquinorbornene system is modified an asymmetry is introduced and the magnitudes of the above effects might be evaluated. In addition to the structures already in the literature, we will report on a low temperature investigation of anti-sesquinorbornene, several derivatives in which the ethylene bridge has been modified by substitution and on several syn-oxabenzosesquinorbornene structures. The results of molecular mechanics and quantum mechanical calculations will be compared with the experimental data.

04.1–17 THE CONFORMATION OF PROLINE USING THE CONCEPT OF PSEUDOROTATION. By K.K. Chacko, Veena Ravichandran and S. Swaminathan, Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras - 600 025, India.

Conformational analysis of proline based on the usual best plane method is only an approximate way of defining its true conformation. A more rigorous approach is to use the concept of pseudorotation applied to the five membered pyrrolidine ring system. The procedure for the calculation of the pseudorotational parameters 'P' (Phase angle) and '$\tau_m$' (maximum amplitude of pucker) from the endocyclic torsion angles of the ring system and the method of representation of its conformation by making use of the pseudorotational pathway chart are already available (Chacko, Swaminathan and Veena (1983) Curr. Sci., 52, 660).

Here we make use of the crystallographic data (from the Cambridge Data file) consisting of over 120 prolyl residues in peptides and cyclic peptides to carry out a detailed analysis on the conformation of proline using the concept of pseudorotation. The results of the analysis bringing out the salient features of the mode of puckering of the pyrrolidine ring system will be presented.

04.2–2 ANGULAR PREFERENCES OF INTERMOLECULAR FORCES AROUND HALOGEN CENTERS: DIRECTIONAL ANISOTROPY OF "ELECTROPHILIC AND "NUCLEOPHILIC" APPROACH AROUND HALOGENS AND "ELECTROPHILE-NUCLEOPHILE" PAIRING IN HALOGEN···HALOGEN INTERACTIONS.* By N. Ramasubbu and R. Parthasarathy, Center for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, New York 14263, USA.

During our studies of Se···Se interactions in diselenides (Ramasubbu and Parthasarathy (1983) Amer. Cryst. Assn. Series 2, 11, pc8), we noticed that halogen atom X of a few R-X groups engage in two types of contacts: (i) with Se in a "head-on" fashion i.e., the Se atom approaches X on the back-side of the R-X bond and the selenide plane normal to R-X and (ii) "side-on" fashion when Se approaches X nearly normal to the R-X bond, and X approaches Se along the backside of Y-Se or Z-Se of selenides. These results suggested preferred direction of "electrophile" (E) and "nucleophile" (Nu) approach around halogen centers. Hence, we analyzed the crystallographic environment of halogen centers (C-X, X = Cl, Br, I) (Murray-Rust and Motherwell (1979) J. Am. Chem. Soc. 101, 4374) using structural data contained in the Cambridge Crystallographic Data Base and locally modified version of GEOM78. We limited our analysis to monovalent halogens of the C-X group and to distances equal to or less than the sum of the van der Waals' radii of contacting atoms. We also focused on "strong interactions" showing the closest approach (Δr is most, $\Delta r_{Nu} = r_X + r_{Nu} - d_{X...Nu}$; $\Delta r_E = r_X + r_E - d_{X...E}$; $\Delta r_X = 2r_X - d_{X...X}$) assuming that weaker interactions to the same halogen atom are consequences of the stronger ones. We find that, in general, "electrophiles" tend to approach the halogen centers at an angle θ(<C-X···E) approximately equal to 90° and "nucleophiles" at ≈ 180°. When there are no dominant interactions of X with an "electrophile" or a "nucleophile" ($\Delta r_{Nu}$ or $\Delta r_E < \Delta r_X$) $C_1$-$X_1$...$X_2$-$C_2$ interactions fall into two groups: (a) Types I and II with "electrophile-nucleophile" pairing as characterized by two angles $\Theta_1$ ($<C_1-X_1...X_2$) ≈ 90° and $\Theta_2$ ($<C_2-X_2\cdots X_1$) ≈ 180° 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.

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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 cyclation processes of gallicin 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, Dc=1.18 g.cm-3, μ(CuKα)=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 gallicin and other germacranolides. The lactone ring is envelope conformated, 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 gallicin (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.

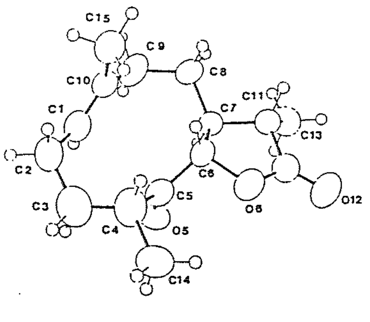


Figure 1.

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. Org. 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, Dc=1.41 g cm-3, μ(MoKα)=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, occuring 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 g1 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 g1 conformation, because the steric hindrance would prevent the eclipsed conformation, 3) the o-substitution obliges to a rigid positionement of the -C≡N function, which cannot rotate closer to the o-group. Rotation in opposite sense is prevented by the dipole charge enhancement mentioned above.

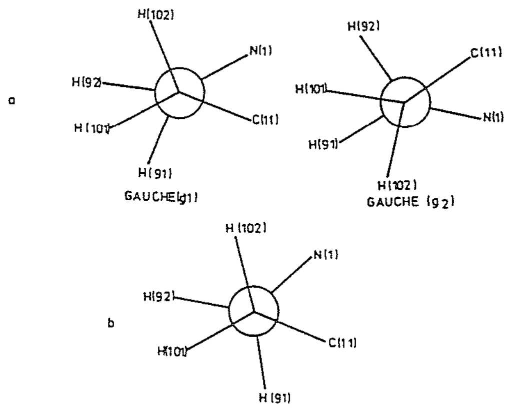


Fig. 1

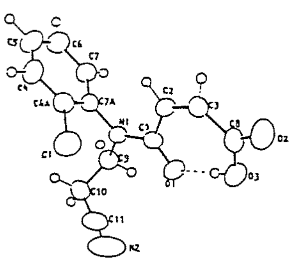

Fig. 2