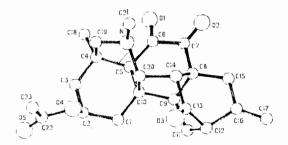PS–06.06.13 CRYSTAL AND MOLECULAR STRUCTURE OF VILMORINONE. By Zhou Zhong–yuan*, Yu Kai–bei, Liu Li, Zhou xiang–ge, Analysis and Testing Center of Chengdu Branch, Academia Sinica, Chengdu, China.

Vilmorinone is an effective component of traditional chinese medicine, Aconitum Vilmorinianum Kom., which is distributed over Yunan and Sichuan provinces in China. It is a derivant of Diterpenes, which is used to cure injuries from falls, fractures, contusions and serains as well as rheumatism. Its melting point is 253–255℃, molecular formula is $C_{24}H_{29}NO_5$. The sample is purified and recrystalized several times, but only twin crystals were got.

A selected crystal with dimension about $0.46 \times 0.60 \times 0.42mm^3$ was examined on R3M/E four–circle diffractometer. The crystal is transparent, but there is a demarcation line in center, so it is a twin crystal. The two basic single crystal of the twin are not the same size, one is bigger and the other is smaller. They are connected with the rotation angle of 165°. Using the CHDU programme for determining cell of twin crystal determined parameters of basic single crystal of the twin. 25 diffraction peaks were found, but only 14 of them had benn indexed and primary parameters of crystal cell were determined. In the area of $15 < 2\theta < 25°$, about 200 reflections were collected by the method of Wyckoff scan, at the speed of 57.3°, in which 25 stronger reflections were selected and centered again to determine accurate paramenters of crystal cell: a=8.012(3), b=13.696(6), c=18.273(8)Å, $\alpha = \beta = \gamma = 90°$, V=2005.3(1.5)Å. Space group is $P2_12_12_1$, Z=4. Diffraction data of 3016 unique reflections were collected, and observed reflections of 2642 with $I > 3\sigma(I)$. LP and absorption correction were applied.

Strcture analysis of Vilmorinone shows that title compound is a five–ring compound and has a structure unit of adjacent Diketones, which it is rare in Diterpenoid Alkaloid. It is interesting that the double bond of carbon–oxygen between C(6) and O(1) (1.218Å) is longer than between C(7) and O(2) (1.191Å). Maybe, The reason is that the distance between C(6) and N atoms is shorter (2.514Å), which cause a little conjugate effect of leap over ring, so the double bond C(6)–O(1) tends a litile toward single bond and make the bond of carbon–oxygen longer. Effect of leap over ring is very common in the solution of the similar alkaloid. Experiment has proved that there is also such effect under the condition of crystal state.

PS-06.06.14 SYMMETRY–MODIFIED MAPPING AND CLASSIFICATION OF SEVEN– AND EIGHT–MEMBERED RING CONFORMATIONS USING CRYSTALLOGRAPHIC DATA by Frank H. Allen, Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK & J.A.K.Howard and Nigel A. Pitchford*, Department of Chemistry, Durham University, Durham DH1 3LE, UK

Knowledge of the potential energy hypersurface for a chemical fragment in terms of global or local energy minima and possible low–energy (interconversion pathways) is of fundamental chemical and structural interest. Nowadays, such knowledge is vital in model building aimed particularly at rational drug design. The required information may be obtained through analysis of the geometric variations that occur in the available crystallographic observations of the fragment, since these observations are likely to be aligned closely with the low–energy features of the relevant conformational hypersurface. With more than 100,000 organic carbon structures now in the Cambridge Structural Database (CSD) several hundreds of observations may be available for a common fragment. Thus statistical and numerical methods must be used to organise these data and recognise patterns and relationships that occur within them.
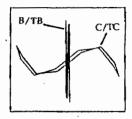
We have used symmetry–modified principal component and cluster analyses to map and classify the observed conformations of both cycloheptane and cyclooctane ring systems. Cycloheptane geometry was described by 7 intra–annular torsion angles. Each ring of D_{7h} topological symmetry has 28 conformational equivalents which fill a four dimensional hypersurface. Principal component analysis of the torsional 7–space reveals the expected four PC's which exist as two degenerate pairs: one pair associated with the chair twist–boat pathway. The PC "scores" can be directly correlated with the Cremer–Pople (J.Am.Chem.Soc., 1975,97,1354–1358) description of ring pucker. Pseudorotation pathways describe helical tracks on toroidal surfaces (Figure 1). Symmetry–modified cluster analysis dissects the dataset into four significant clusters corresponding to twist–chair, chair, flattened twist–chair and twist–boat conformations respectively. The effects of endo–unsaturation and of common external substituents on the conformation of the seven–membered ring are also presented.

Cyclooctane rings exhibit D_{8h} topological symmetry and are here described in terms of their eight intra–annular torsion angles. Each ring has 32 conformational equivalents which occupy a five–dimensional hypersurface, and the idealized symmetrical conformations of the rings lie on five characteristic

pseudorotation pathways as described by Evans and Boeyens (Acta Cryst. 1988, B44, 663–671). Previous energy calculations have found the BC/TBC itinerary to be the lowest lying on these five pathways, with the TBC conformer at 7.1 kjmol^{-1} above the global minimum BC form. Symmetry–modified principal component and cluster analyses were used to map and classify all observed conformations of the cyclooctane rings: BC conformers being predominant, with the only other significant cluster populations belonging to other conformations on the BC/TBC pseudorotation itinerary. The dominance of the BC conformation becomes less marked when the analysis routines are extended to encompass all other 8–membered ring systems.

The relationships between chemical structure, environment and conformation for both seven– and eight–membered systems will be discussed.
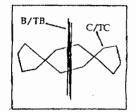
Figure 1. A model of the C/TC and B/TB pseudorotation ilineraries