Present work intends to quantify the degree of isostructurality of these pairs by means of packing coefficients, hydrogen bond parameters and analysis of the corresponding atomic coordinates of eleven steroids possessing a common flexible 14-iso-aethiocholane skeleton. E.g. scillarenin (reported by us earlier as 3β,14-dihydroxy-14β-bufa-4,20,22-trienolide, Ribár et al (1983) J.Chem. Res.(S) 90) is quasi-isostructural with bufalin (Rohrer et al (1982) Acta Cryst. B38, 1865) although there is a quite relevant difference between the puckering of their A rings.

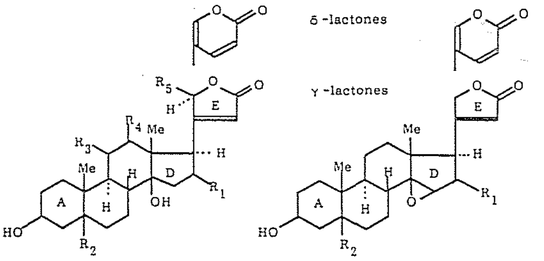

Fig. 1. Eleven steroids having a common sp. gr. $P2_12_12_1$

γ-lactones

DIGITOXIGENIN* DIGIREZIGENIN
METHYLDIGITOXIGENIN: R_5= Methyl
5β-HYDROXYGITOXIGENIN: R_1=R_2= OH

δ-lactones

BUFALIN CINOBUFAGIN: R_1= O-Acetyl
BUFOTALIN: R_1= O-Acetyl CINOBUFOTALIN: R_1= O-Acetyl
GAMABUFOTALIN: R_3= OH R_2= OH
ARENOBUFAGIN: R_3=OH, R_4= O=
SCILLARENIN: Δ 4,5-ANHYDROBUFALIN
* No special indication is given if R_i = H.

04.1-4 CONFORMATION OF DIPHENYLSULPHIDE DERIVATIVES

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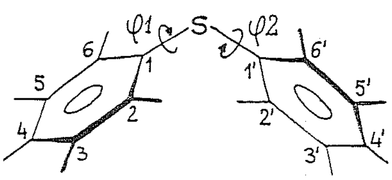
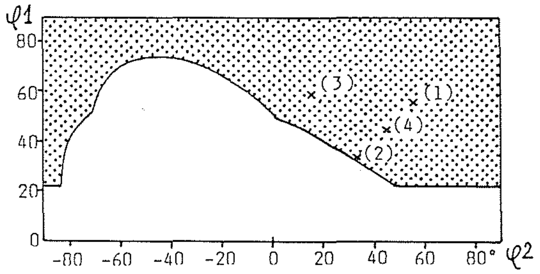
In the present paper we would like to discuss the conformation of diphenylsulphide derivatives, the basic structures in the chemistry of alkyl-aryl-sulphuric compounds. A diphenylsulphide molecule (1) contains two rigid fragments - phenyl rings - which can rotate about its "soft" S-C bonds.



(1)

The conformation of the molecule can be conviniently described by torsion angles C(1')-S-C(1)-C(2) [$\varphi1$] and C(1)-S-C(1')-C(2') [$\varphi2$] or, in other words, by the angles between the plane containing atoms C(1)-S-C(1') and the planes of the phenyl rings. The rotations of the phenyl rings about the S-C bonds are limited by the steric hindrances due to the intramolecular van der Waals contacts. A simple computer program was written to evaluate these contacts as a function of $\varphi1$ and $\varphi2$. In that program the steric hindrances in the diphenylsulphide molecule were defined by means of van der Waals radii, thus the conformations accepted of the two phenyl rings larger than the sums of the appropriate van der Waals radii [1.6 for carbon and 1.0 Å for hydrogen atom]. It was demonstrated that the steric hindrances in this molecule is due to the interactions of ortho-hydrogen atom H(2) [or H(6)] with atoms H(2'), C(2'), C(1'), C(6') and H(6').

In the plot presented below the dotted area show the possible values of $\varphi1$ and $\varphi2$. The plot also shows the conformations of four diphenylsulphide derivatives determined experimentally:
(1.) diphenylsulphide, $\varphi1$= $\varphi2$=55.6° (Rozsondai et al., Acta Chim. Budapest 1977, 94, 321);
(2.) 4,4-thiodibenzylothiol, $\varphi1$= $\varphi2$=33.4° (Ratajczak-Sitarz et al., Acta Cryst. C - in press);
(3.) 1,4-bis(phenylthio)benzene, $\varphi1$=14.9°, $\varphi2$=59.2° (Andreetti et al., Cryst. Struct. Comm. 1981, 10, 789);
(4.) crystalline phase of poly-p-phenylenesulphide, $\varphi1$= $\varphi2$=45° (Tabor et al., Eur. Polym. J. 1971, 7, 1127).
In three of these structures the phenyl rings are related by the twofold axis passing through the central S atom and, consequently, $\varphi1$ and $\varphi2$ have the same values. The plot shows that angles $\varphi1$ and $\varphi2$ in all above structures fall in the region least limited by steric hindrances, where $\varphi1$ and $\varphi2$ have the same sign. The close van der Waals contacts were found only in the molecule of 4,4-thiodibenzylothiol: H(2)...C(2') of 2.71(6) Å.



04.1-5 THE RELATIONSHIP BETWEEN THE Br···O SEPARATION AND Br-C-C=O TORSION ANGLE IN ALPHA-BROMOCYCLOHEXANONE RINGS.

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The Br-C-C=O torsion angle in an α-bromocyclohexanone ring can have several values: it can be 0° or 120° in an ideal chair, while in an ideal boat it can be 0°, 60° or 120°. If the ring is an ideal twist boat, then torsion angles of 30° and 90° are possible. However, with the flexible boat form any torsion angle between 0° and 180° is possible. A series of structures containing the α-bromocyclohexanone system (Sommerville, Laing, Acta Cryst., 1976 B32, 2683, 2685, 2687; 1978, B34, 1736), showed that there was a discontinuity in the relationship between the Br-C-C=O torsion angle and Br···O distance at about 50°, below which the Br···O distance remained effectively constant at about 3.0Å, (Fig). This effect is caused by the non-compressibility of the van der Waals radii of the Br and O atoms. Analysis of the parameters of all compounds of this class in the Cambridge Data File showsthe same phenomenon. Below a torsion angle of about 50° the Br···O distance is approximately constant. This is a result of the internal Br-C-C and C-C-O angles being forced open to accomodate the compression strain as the torsion angle is reduced. An approximate value of the Br···O distance can be estimated for any torsion angle Θ by the equation:

$$d^2 = R - S\cos\theta + T\cos^2\theta$$

where R = 11.73, S = 3.62, T = 0.75