

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

09.2-30 CONFORMATION OF 10-HETEROARYLPHENOTHIAZINES. By Shirley S. C. Chu, Patrice de Meester, and Robert D. Rosenstein, School of Engineering and Applied Science, Southern Methodist University, Dallas, Texas 75275, U. S. A.

The crystal structures of a number of 10-heteroarylphenothiazines have been determined by the single crystal x-ray diffraction method. Phenothiazine is a tricyclic compound with the central ring in a boat conformation. The objectives of this study are to determine the effects of the nature and position of the substituents on (1) the conformation and configuration of the phenothiazine ring system, and (2) the conformation of the 10-aryl group with respect to the phenothiazine ring. The structures of 10-(2'-pyrazyl)phenothiazine (I), 10-(4'-nitrophenyl)phenothiazine (II), 10-(2'-nitrophenyl)phenothiazine (III), 10-(2'-methoxyphenyl)pyrido[3,2-b][1,4]benzothiazine (IV), 10-(2'-pyrido)pyrido[3,2-b][1,4]benzothiazine (V), and 10-(4'-dimethylaminophenyl)pyrido[3,2-b][1,4]benzothiazine (VI) will be reported. The plane of the 10-phenyl or 10-pyrido ring in (III), (IV), (V), and (VI) is nearly parallel to the plane bisecting the tricyclic ring. However, the plane of the 10-pyrazine ring in (I) and the plane of the 10-phenyl ring in (II) are nearly perpendicular to the plane bisecting the tricyclic ring. The electronic interaction between the π -deficient 10-substituent and the tricyclic ring can only occur with the conformation of the ring system observed in (I) and (II). This interaction can be demonstrated by the changes in bond lengths and bond angles involving the bond which links the two ring systems.

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09.2-31 THE STRUCTURES OF BENZO[b]THIOPHEN DERIVATIVES. By Z. Ali-Adib, A. Rawas and H.H. Sutherland, Physics Department, University of Hull, Hull, HU6 7RX, England.

The structures have been solved by Patterson syntheses using equi-inclination Weissenberg data.

I. 2-methyl-benzo[b]thiophen, C_9H_8S , orthorhombic $a = 11.71(1)$, $b = 11.031(1)$, $c = 5.96(1) \text{ \AA}$, $Z = 4, Pna2_1$, $D_m = 1.27$, $D_x = 1.28 \text{ Mg m}^{-3}$, $CuK\alpha$, $T = 283 \text{ K}$, $R = 0.08$ for 553 independent reflections. The five and six membered rings are planar and inclined to one another at 1.0° . The average C-S bond is $1.755(16) \text{ \AA}$, the C-S-C angle is $92.0(7)^\circ$.

II. 2,3-dibromo-benzo[b]thiophen, $C_8H_4Br_2S$, monoclinic, $a = 3.95(1)$, $b = 15.15(1)$, $c = 14.41(1) \text{ \AA}$, $\beta = 92.0(1)^\circ$, $Z = 4 P2_1/c$, $D_m = 2.22$, $D_x = 2.25 \text{ Mg m}^{-3}$, $T = 285 \text{ K}$, $R = 0.09$ for 806 independent reflections. The five and six membered rings are planar and inclined to one another at 0.7° . The average C-S bond is $1.704(25) \text{ \AA}$, the C-S-C angle is $91.1(12)^\circ$, the average Br-C bond is $1.838(22) \text{ \AA}$.

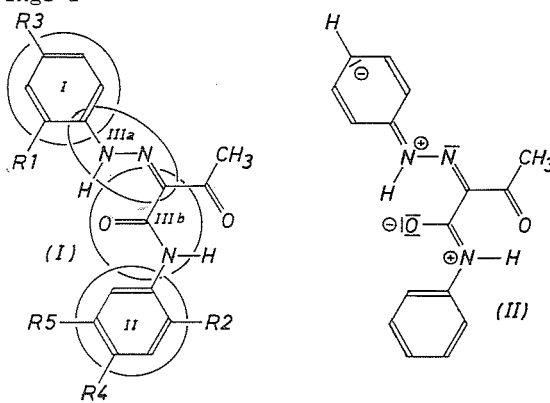
III. 2,3-dichloro-benzo[b]thiophen, $C_8H_4Cl_2S$, monoclinic, $a = 3.89(1)$, $b = 14.97(1)$, $c = 14.20(1) \text{ \AA}$, $\beta = 92.0(1)^\circ$, $Z = 4 P2_1/c$, $D_m = 1.63$, $D_x = 1.63 \text{ Mg m}^{-3}$, $T = 285 \text{ K}$, $R = 0.09$ for 1054 independent reflections. The five and six membered rings are planar and inclined to one another at 1.0° . The average C-S bond is $1.761(10) \text{ \AA}$, the C-S-C bond is $90.0(5)^\circ$, the average Cl-C bond is $1.728(10) \text{ \AA}$.

IV. benzo[b]thiophen, C_8H_6S , orthorhombic $a = 7.82(1)$, $b = 5.87(1)$, $c = 14.88(1)$, $Z = 4, Pna2_1$, $D_m = 1.29$, $D_x = 1.31 \text{ Mg m}^{-3}$, $T = 281 \text{ K}$

The five and six membered rings are planar.

09.2-32 DERIVATIVES OF HYDRAZONE OF ACETOACETYL ANILIDE. By E. F. Paulus and W. Rieper, Hoechst AG, D-6230 Frankfurt/M 80, FRG

The crystal structure of 12 compounds with the general formula (I) was investigated by X-ray. The table gives the ligands R and the angles between the central planes III and the phenyl-rings I



| | R1 | R2 | R3 | R4 | R5 | \angle I/IIIa | \angle II/IIIb |
|------|------------------|------------------|------------------|------------------|------------------|-----------------|------------------|
| (1) | OCH ₃ | H | H | H | H | 4.0 | 11.5 |
| (2) | CH ₃ | OCH ₃ | H | H | H | 1.1 | 7.9 |
| (3) | H | CH ₃ | H | H | H | 3.6 | 6.2 |
| (4) | CH ₃ | H | H | H | H | 1.7/11.4 | 18.8 |
| (5) | OCH ₃ | CH ₃ | H | H | H | 1.2/1.5 | 14.7/1.7 |
| (6) | H | OCH ₃ | H | H | H | 4.9 | 14.0 |
| (7) | NO ₂ | H | CH ₃ | H | H | 5.4 | 8.6 |
| (8) | H | H | H | H | H | 2.1 | 12.1 |
| (9) | H | H | OCH ₃ | OCH ₃ | H | 7.2 | 2.5 |
| (10) | CH ₃ | CH ₃ | H | H | H | 7.7 | 1.7 |
| (11) | OCH ₃ | OCH ₃ | H | H | H | 2.9 | 23.0 |
| (12) | NO ₂ | OCH ₃ | CH ₃ | Cl | OCH ₃ | 10.5 | 3.1 |

and II respectively. It can be seen that in the unsubstituted compound the phenylring on the hydrazone group puts up a definitely smaller angle than the phenylring on the other side of the molecule. The same is the case, when R₁ and R₂ are identical and the rest of the substituents are H-atoms. Do we have other substituents in para-positions (and to a certain amount also in ortho-positions), which are able to spend electrons to the phenylrings, then we get a different effect on the angles between the groups: The angle between the phenylring at the hydrazone and the central group gets larger, whereas the angle between the anilide ring and the central group gets smaller. The given resonance formula(II) may be an explanation for these effects.

This mesomeric form is helping to stabilize the planarity of the molecule. Substituents which are donating electrons to the phenylring are stabilizing in the mesomeric form(II) the anilide part, but destabilizing the hydrazone part.

When there are two molecules in the asymmetric unit like in the compounds (4) and (5), these rules are obeyed only by one of them. The other one, which is connected to the first one by a noncrystallographic pseudocentre of symmetry, shows an appreciable distortion, never the less the surroundings of the two molecules in the crystal are almost the same. An explanation can be that the methyl group can flatten and at the same time distort a molecule by steric hindrance what seems to be the case also in solution - and this again is the reason for the two molecules in the asymmetric unit. The distances of the H-atom of the NH-groups and the C-atom of the methyl groups are extremely short and are ranging from 2.41 to 2.54 Å.