

09.2-10 CRYSTAL STRUCTURE OF AN ASSYMETRIC HIGHLY CHLORINATED DIACETYLENE MONOMER, $C_{12}H_4OCl_6$.

by
E. Molins and C. Miravittles
Institut de Ciència de Materials. (C.S.I.C.)
c/ Martí i Franqués, s/n. Apartado de Correos 30102.
08028 BARCELONA. Spain.

and
J. Veciana
Departament de Materials Orgànics Halogenats. Centre
d'Investigació i Desenvolupament. (C.S.I.C.)
c/ Jordi Girona Salgado, s/n. 08034 BARCELONA. Spain

In our research work on polyconjugated polymers we have undertaken the study of diacetylenes and polydiacetylenes.

A very pale yellow crystal of the title compound was selected for X-ray diffraction analysis to establish its crystal structure. The compound crystallizes in the $P2_1/c$ space group with $a = 4.056(3)$, $b = 23.429(4)$, $c = 15.029(2)$ Å, $\beta = 91.26(2)^\circ$, $V = 1431.7$ Å³. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer; from 2508 unique reflections, 1590 were considered observed ($F > 2\sigma(F)$). The structure was solved with MULTAN-11/84 (Main et al., 1984) and refined with SHELX-76 (Sheldrick, 1976) up to a final R of 0.039 and R_w of 0.044.

The crystal packing consists of a parallel stacking of 6-chloro-2,4-hexadiinyl pentachlorophenyl ether along the x -axis. Diacetylene groups form an angle of 66.9° with this axis.

Financial support from C.S.I.C. (Grant 603/846) is gratefully acknowledged.

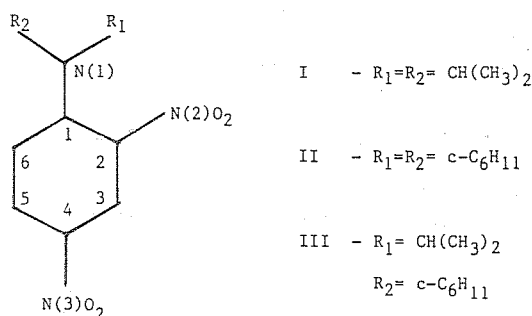
09.2-11 INTRAMOLECULAR $S \cdots O$ INTERACTIONS IN N,N' -DIMETHYL-2,2'-DITHIODIBENZAMIDE AND N -METHYL-2-(BENZYL-SULFINYL)BENZAMIDE. By F. Iwasaki, N. Toyoda and N. Yamazaki, Dept. of Materials Science, The Univ. of Electro-Communications, Chofu-shi, Tokyo 182, Japan.

The structures of the title compounds were determined by an X-ray method in order to investigate the hypervalency of sulfur. Crystal data: (I, 292K) Monoclinic, $C2/c$, $a = 18.643(4)$, $b = 4.9147(7)$, $c = 18.696(5)$ Å, $\beta = 112.43(2)^\circ$, $Z = 4$, $R = 0.036$ (1625 reflections, $2\theta \leq 55^\circ$), (I, 173K) $C2/c$, $a = 18.419(3)$, $b = 4.9120(6)$, $c = 18.578(5)$ Å, $\beta = 112.45(2)^\circ$, $Z = 4$, $R = 0.046$ (3716, $2\theta \leq 85^\circ$), (II) Orthorhombic, $Pcab$, $a = 16.118(3)$, $b = 12.403(2)$, $c = 14.205(2)$ Å, $Z = 8$, $R = 0.055$ (2285).

The molecule (I) has an exact two fold axis bisecting the S-S bond. The torsion angle of C-S-S-C is 88.0° . In (I) and (II) weak intramolecular interactions are found between S and O of the amido group. The $S \cdots O$ lengths are 2.890 and 2.712 Å for (I, rt) and (II), respectively, which are longer than those in the typical thiathiophthene-like $S \cdots O$ compounds (1.9 Å) but are shorter than the sum of van der Waals' radii for S and O (3.25 Å). The angle of $S-S \cdots O$ is 173.5° for (I) and that of $O-S \cdots O$ for (II) is 173.4° . The dihedral angle of the amido plane and the benzene ring are 44.3 and 20.2° for (I) and (II), respectively. The molecules of (I) are linked by the $N-H \cdots O=C$ intermolecular hydrogen bonds elongated along the b axis. The molecules of (II) are also linked by the $N-H \cdots O=S$ hydrogen bonds forming a zig-zag chain elongated along the c axis. The lengths of $N \cdots O$ are 2.813 and 2.845 Å for (I) and (II), respectively. Electron-density distributions will be shown using the intensity data at 173K.

09.2-12 GEOMETRY STUDIES OF N -DISUBSTITUTED 2,4-DINITRO ANILINES. EFFECT OF BULKY SUBSTITUENTS. G. Punte and B. E. Rivero, Depto. de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata and S. Socolovsky and N. S. Nudelman, Depto. de Química Orgánica, Facultad de Ciencias Exactas, Universidad de Buenos Aires, Buenos Aires, Argentina.

The substances that have been selected to study the influence that bulky substituents have on the molecular geometry are shown in the figure.



Although there is relatively abundant literature on N -unsubstituted nitroanilines, reports on the geometry of heavily hindered nitroanilines are scarce, probably because they are difficult to synthesize.

From X-ray single crystal analysis (to be published elsewhere) some features in molecular geometry, shared by the three compounds, can be observed.

There is an appreciable aromatic ring distortion: C(1) endocyclic angle decrease (mean value: $113.4(9)^\circ$) this effect is accompanied by a lengthening of C(1)-C(2) and C(1)-C(6) bond lengths (1.422(9) and 1.417(6) Å) and by an increase in C(2) and C(6) angles ($123.9(8)$ and $122.9(1)^\circ$). The lack of planarity of the ring that can be assessed from the best least-squares plane X^2 values is mainly due to the substituents on C(1), mean C(1) atom distance to mean plane is bigger than three e.s.d.

The nitro groups bond angles show the existence of repulsion between both oxygens. The influence of the hindrance in the group in the ortho position can be clearly seen through the higher dispersion found for bond distances and angles and the rotation of the nitro group out of the ring plane, dihedral angle ranges from $37.4(2)$ to $55.8(4)^\circ$.

The analysis of the values observed for the angles between the C-N bonds and the mean plane of the ring shows that C(4)-N(3) bond might be considered coplanar ($1(1)^\circ$) while C(2)-N(2) and C(1)-N(1) are out of the plane ($12(2)$ and $7(1)^\circ$). The last figure plays an important role in the interpretation of spectroscopic and reactivity behaviour of these compounds.

The results found from solid state studies are related with ^{13}C nmr and ultraviolet spectroscopic data in solution (to be published).