PS06.00.16 CRYSTAL STRUCTURE OF AROMATIC DIACETYLENE DERIVATIVES AND REACTIVITY OF SOLID-STATE POLYMERIZATION Y.Shibamoto*, K.Yano, N.Kanehisa, Y.Yamamoto†, S.Tagawa†, Y.Kai, Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan, †The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan

Some diacetylene compounds are known to undergo solid-state polymerization upon heating, irradiation or mechanical stimulation, and give single crystals of conjugated polymer. The reactivity of a diacetylene in the crystalline state is governed by the molecular packing of the monomer. Only those diacetylenes which have suitable packing conditions will undergo facile polymerization. The single crystals of these conjugated polymer have attracted attention on their physical properties, such as conductivity, optical nonlinearity, and mechanical strength.

We have investigated the correlation between the crystal structure and the reactivity in solid-state polymerization of various aromatic acetylene derivatives. We reported the crystal structures of some diethynylbenzene derivatives and interpreted the characteristic features of them in the solid-state polymerization upon irradiation with gamma-ray based on the unique monomer packings (Y.Kai, A.Yamamoto, D.Xu, N.Kasai, M.Hagihara, Y.Yamamoto, S.Takahashi and K.Hayashi, *Makromol. Chem.* 1987. **188**, 3047-3059). Recently, we have synthesized the aromatic diacetylene derivatives, 1-(5-hydroxypenta-1,3-diynyl)-4-ethynylbenzene(I), 1,4-bis-(5-hydroxypenta-1,3-diynyl)-benzene(II), and 1,2-bis-(5-hydroxypenta-1,3-diynyl)-benzene(III), and obtained these single crystals. So the crystal structures of I, II and III were determined by X-ray diffraction method. As a result, it was found that the monomer molecules in the crystals of both I and II take suitable packing structures to undergo solid-state polymerization, but in the crystal of III, the monomer molecules are arranged not so as to undergo solid-state polymerization. With respect to the crystal of I, monomer arrangement is suitable for solid-state polymerization not only between diacetylene moieties but also ethynyl ones. The distance between the neighboring ethynyl moieties is nearer than that between diacetylene ones. So stepwise polymerization may be reasonable, first between ethynyl moieties, next between diacetylene ones.

PS06.00.17 MOLECULAR AND CRYSTAL STRUCTURES OF DONOR - ACCEPTOR SUBSTITUTED POLYENES INVOLVING 1,3-INDANDIONE AND DIBENZOCYCLOHEPTENEDIONE MOIETIES. Vladimir Khodorkovsky[1], Arkady Ellern, Ben-Gurion University of the Negev, Chemistry Dept., P.O.B. 653, Beer Sheva, Israel.

Donor-acceptor substituted polyenes present currently a subject of numerous investigations due to their nonlinear optical properties. The importance of specific structural features in such chromophores for efficient second harmonics generation has been established, in particular, within the frame of 'bond length alternation' (BLA) approach.

Derivatives involving the electron accepting moiety of 1,3-indandione and its structural analogs are often photoconducting and possess moderate to strong nonlinear optical properties. Many derivatives are distinguished by their ability to form several polymorphic modifications. For instance, for 2-(p-dimethylaminobenzylidene)-1,3-indandione, yellow-orange in solutions, two red and one blue polymorphs are known.

Recently we have synthesized a series of 2-ylidene 1,3-indandione and dibenzocycloheptenedione derivatives and determined their crystal structures. The deep color in solid state apparently can not be explained by enhanced intermolecular interactions and no considerable difference in BLA patterns has been found. The results of our crystallographic and quantum mechanical calculations which can explain the tendency for polymorphism and deep color in solid state within this class of compounds will be presented.

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PS06.00.18 STRUCTURAL STUDIES OF INTERMEDIATES IN A NOVEL SYNTHESIS OF ARYLOXYPROPIONONITRILES. J. Ellena[1,3], G. Punte[1], J.C. Autino[2], G.P. Romanelli[2] and A.E. Goeta[4]. [1]PROFIMO. Depto. de Física, Facultad de Ciencias Exactas, UNLP, Argentina, [2]LADECOM, Laboratorio de Estudio de Compuestos Orgánicos, Facultad de Cs. Exactas, UNLP, Argentina, [3]Facultad de Ingeniería, UNLP, Argentina, [4]Durham Chemical Crystallography Group, Chemistry Department, University of Durham, UK.

3-Aryloxypropiononitriles are important synthetic intermediates for compounds of biopharmacological and technological uses, such as enzymatic inhibitors, antijuvenile hormones for plague control, biocides, useful polymers, compounds used in the leather industry, etc. A novel synthesis of 3-aryloxypropiononitriles, avoiding the use of contaminants, has proved to give good yields for small substituents[1]. The compounds **2- and 4-(2-bromoethoxy)diphenylmethanes** (**I** and **II** respectively) have been synthesized as part of a general study on the goodness of the synthetic method to handle bulky substituents. No significant changes in the crystal structures of I and II have been observed in going from R.T. to 150K. The molecular conformation of **I** and **II** in solid state, obtained from single crystal X-ray difractometric data at low temperature, are compared. The observed differences are analyzed and the conclusions correlated with solution R.T. ^{1}H and ^{13}C nmr data. Variations in the m.p. as a function of the substituents position are analyzed in terms of the different molecular packing.

[1] A.A. Vitale, G.P. Romanelli, J.C. Autino and A. B. Pomilio. *J. Chem. Res. (S)*, 1993, 386-387.Å

PS06.00.19 CRYSTAL AND MOLECULAR STRUCTURE OF 2,10 DICHLORO 6-TRICHLOROMETHYLDIBENZO [d,g] [1,3,6,2] DIOXATHIAPHOSPHOCIN 6-OXIDE. N. Jagadeesh Kumar, T. V. Narasaiah, M. Krishnaiah, Department of Physics, Sri Venkateswara University, Tirupati-517 502, INDIA

The crystal structures and conformations of organophosphorus compounds have become the subject of intense study due to their involvement in many biological processes(Corbridge, 1977; Emsley & Hall, 1976 and Sankara Reddy & Devendranath Reddy, 1995). To our knowledge there have been few reports on structural studies of 8-membered heterocyclic organophosphorus compounds with sulfur as one of the endocyclic atoms which prompted us to undertake the crystal structure determination of [1,3,6,2] dioxathiaphosphocin derives to know their molecular and conformational change with respect to the different oxocyclic substituents.

Crystals of title compound obtained from 2-propanol are colourless, monoclinic, $P2_1/n$ with a=11.624(7), b=11.091(3), c=14.407(4)Å, β=107.88(3)°, v=1767.7(12)Å^3, Z=4, ρ_c=1.693Mg/cm^3, λ=0.71073Å, μ(MoKα)=10.37cm^{-1}. The structure has been solved by direct methods (SHELXS 86) using 2652 reflections measured at room temperature on a CAD-4 diffractometer. The refinement by full matrix least-squares method using SHELXL-93 lowered the disagreement factor as R=0.0451 and Rw=0.1093 for 2525 significant reflections [I≥2σ(I)].

The dioxathiaphosphocin ring exhibits a distorted boat conformation which is differing from the expected BC form other similar structures(Mani Naidu et al., 1992, 1994 & 1996).