

and COOH groups in properly chosen positions, have been studied in our Laboratories by X-ray crystallography:

1,4-Dinitrobenzene: Di Rienzo, Domenicano & Riva di Sanseverino, Acta Cryst. B36, 586 (1980).

Terephthalic acid: Triclinic, space group $P\bar{1}$, $a = 5.027$, $b = 5.360$, $c = 7.382$ Å, $\alpha = 115.72$, $\beta = 101.06$, $\gamma = 92.91^\circ$, $Z = 1$, $D_c = 1.587$ g cm⁻³. Refined to $R = 0.0550$ using 630 counter intensities. Further refinement with a larger data set is in progress.

4-Nitrobenzoic acid: Colapietro & Domenicano, Acta Cryst. B33, 2240 (1977).

3-Nitrobenzoic acid: Colapietro, Domenicano & Marciante, God. Jugosl. Cent. Krist. 17, S140 (1982).

3,5-Dinitrobenzoic acid: Colapietro, Domenicano & Marciante, God. Jugosl. Cent. Krist. 17, S140 (1982).

5-Nitroisophthalic acid: Monoclinic, space group $A2/a$, $a = 12.958$, $b = 9.854$, $c = 31.472$ Å, $\beta = 115.63^\circ$, $Z = 16$, $D_o = 1.545$, $D_c = 1.548$ g cm⁻³. Refined to $R = 0.0387$ using 2655 counter intensities.

From the internal ring angles of these molecules the following angular parameters are derived by regression:

NO_2 : $\Delta\alpha = 2.68^\circ$, $\Delta\beta = -1.86^\circ$, $\Delta\gamma = 0.29^\circ$, $\Delta\delta = 0.45^\circ$;
 $COOH$: $\Delta\alpha = 0.01^\circ$, $\Delta\beta = -0.24^\circ$, $\Delta\gamma = 0.01^\circ$, $\Delta\delta = 0.45^\circ$.

Inspection of the residuals shows that in most cases the additivity of angular distortions is respected within experimental error. The largest residual (0.8°) is associated with an unusual environment of a C-H bond. Comparison with previously published angular parameters shows that the values given by Norrestam & Schepper for the COOH group are seriously different from ours, probably due to an inappropriate choice of the data set.

04.1-11 CRYSTAL MODIFICATIONS OF 4-HYDROXYBIPHENYL: THE BIPHENYL STRUCTURE WITHOUT AN INVERSION CENTER AND AN ORDERED STRUCTURE CONTAINING NEARLY PLANAR MOLECULES. By C. P. Brock and K. L. Haller, Department of Chemistry, University of Kentucky, Lexington, KY 40506, USA.

In studying the relationships between crystal packing, molecular geometry, and thermal motion for some simply substituted biphenyls, we have discovered several structures of 4-hydroxybiphenyl (hereafter, BIPHOH) that shed light on the problematic structure of the parent molecule.

One polymorph of BIPHOH is almost isostructural with the room-temperature form of biphenyl (and 4,4'-dihydroxybiphenyl), but crystallizes in the non-centrosymmetric space group Pa with two full molecules in the asymmetric unit and no imposed symmetry. On the average, the molecules are nearly planar (the twist angles ψ are both less than 5 deg), but the structure, like those of the linear polyphenyls, is affected by large-amplitude thermal motion and/or disorder. At room temperature there are satellite spots around the h0l Bragg peaks in directions perpendicular to the long molecular axes and corresponding to spacings of ca. 39 Å.

A second polymorph of BIPHOH contains two independent molecules (space group $P2_12_12_1$) with ψ values of 2.3(2) and 2.0(3) deg and no indication of disorder. At room temperature the average mean-square libration $\langle L^{22} \rangle$ about the long molecular axis is 72(6) deg². The 1:3 complex of BIPHOH with 4,4'-dinitrobiphenyl also contains nearly planar [$\psi = 0.5(5)$ deg] BIPHOH molecules that have similar L^{22} values. These librational amplitudes are not much larger than those observed at room temperature for the 4,4'-dinitrobiphenyl molecules in the complex [$\langle L^{22} \rangle = 34(4)$ deg²; $\psi = 37, 37, 37$ deg], or for the well-ordered structures of 4,4'-dichlorobiphenyl [$\langle L^{22} \rangle = 38(2)$ deg²; $\psi = 39, 42$ deg] or 4-biphenylcarbox-

ylic acid [$\langle L^{22} \rangle = 50(5)$ deg²; $\psi = 29, 36, 32$ deg].

These results support two conclusions. First, the static and/or dynamic disorder observed for the high-temperature phases of the linear polyphenyls is not a consequence of the crystallographically-imposed inversion symmetry (which is absent for the Pa modification of BIPHOH), but is rather a product of the overall crystal packing arrangement. Secondly, the wide distributions associated with the atomic positions of the linear polyphenyls are not necessary results of the molecules' crystallizing with $\psi=0$ deg. Relatively narrow distributions are found for BIPHOH in the $P2_12_12_1$ modification and in the complex.

Low-temperature studies of these structures are in progress.

* Cailleau, Baudour, Meinel, Dworkin, Moussa & Zeyen (1980). Faraday Discuss. Chem. Soc., 7-18.

This work was supported by the Petroleum Research Fund of the American Chemical Society.

04.1-12 PHASES AND PHASE RELATIONS OF RARE EARTH GERMANATES OF COMPOSITION $1RE_2O_3 \cdot 2GeO_2$, RE:La...Lu. By U. Becker and J. Felsche, Fakultät für Chemie, Universität Konstanz, Postfach 5560, 7750 Konstanz, FRG.

Compounds of composition $1RE_2O_3 \cdot 2GeO_2$ show the largest structural variety of rare earth germanates known so far in the two-component systems $RE_2O_3 \cdot GeO_2$, RE:La...Lu. 1:2-germanates display 5 different structure types including two new phases, which we obtained for $Pr_4[Ge_3O_{10}/GeO_4]$ ($P1, Z=6$, $a_0=37.87, b_0=6.948, c_0=6.931$ Å; $\alpha=88.75$, $\beta=90.78, \gamma=95.83^\circ$) and $Ce_4[Ge_3O_{10}/GeO_4]$ ($P1, Z=1, a_0=6.888, b_0=7.058, c_0=7.047$ Å, $\alpha=116.11, \beta=91.35, \gamma=87.66^\circ$). From the large cation effect, rare earths La, Pr, Ce form individual structures, followed by a short sequence of isotopic germanates of Nd, Sm, Eu, Gd. Smaller rare earths Tb...Lu form a long series of isostructural digermanates $RE_2[Ge_2O_7]$. Unique trigermanate anions $[Ge_3O_{10}]^{8-}$ plus monomeric orthogroups $[GeO_4]^{4-}$ dominate the large cation germanates of La...Gd, which show 7-9fold oxygen coordination. The smaller group of lanthanoids Tb...Lu achieve 6-7fold coordination from regular diortho-germanate type anions $[Ge_2O_7]^{6-}$. Thermoanalytical studies reveal monomorphism for germanates of La, Ce, Pr and series Tb...Lu, whereas middle-sized lanthanoid germanates (Nd, Sm, Eu, Gd)₄[Ge_3O_{10}/GeO_4] are dimorphic. Phase transitions occur rather sluggish at temperatures of 800-1200°C. There is one mixed valence/mixed anion phase $Ce^{4+}Ce^{3+}[(GeO_4)_6(Ge_2O_7)_4(Ge_3O_{10})_2]$ with 7fold and 8fold oxygen coordinations of Ce^{4+} and Ce^{3+} -cations, respectively. We discuss special structural features of 1:2 germanates and some corresponding rare earth silicate phases in terms of modulated structures, which allow for an easy approach to structural variance and superstructure characteristics from X-ray single crystal diffraction patterns.