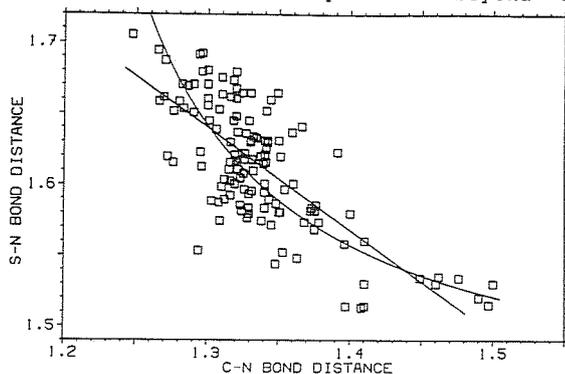if half of the potassium positions are replaced
by sodium, the rest will be looked at as
voids □. From this viewpoint Na□NbCl$_6$ and the
isotypic Na□TaCl$_6$ represent low-symmetry vari-
ants of the K$_2$PtCl$_6$ structure. Among other fea-
tures it is important to note that the sodium
ions and voids occupy alternate layers aligned
parallel to (001).

Despite similar unit-cell dimensions the struc-
ture of Na□SbCl$_6$ differs in two respects. So-
dium atoms and voids □ are found on separate
rods which extend both in c-direction (Wyckoff
positions 2e and 2f); the formation of separate
layers ||(001) is not observed. Another obstacle
is the different orientation of the SbCl$_6^-$ ions.
A related arrangement is however shown by ru-
tile where chains of interconnected TiO$_6$ units
form a three-dimensional network. In the hexa-
chloroantimonate two thirds of these 'octahedra'
remain vacant to comply with stoichiometry,
schematically □□SbCl$_6$. As in the case of tri-
rutile one obtains a threefold superstructure
(space group P 4$_2$/m n m, c' = 3c) with P 4$_2$/m
being an immediate subgroup.

given range of distances. For extrapolation a
better description is provided by a hyperbolic
function d(SN)-d1 = a/ (d(CN)-d2) (k=0.80)
which for very large values of the SN or CN
distances leads to the known CN or SN triple
bond lengths, respectively. Assuming that the
sum in bond order of the two bonds to the
nitrogen equals 3, the following relationships
between bond order and bond distances can be
deduced: d(SN)-1.3 = 0.45/ BO(SN); d(CN)-1.0 =
0.48/ BO(CN).
With respect to the S-N-S system, the correla-
tion between the sum of bond orders (derived
from the respective bond distances by the for-
mula given above) and the enclosed bond angles
is shown in Fig. 2. The least squares line
shown has the form ⪪SNS /30   = BO1(SN) +
BO2(SN) + 1 (k=0.80). A comparable correlation
between bond distances and angles has been
previously proposed by Banister and Durrant (J.
Chem. Res. (S) 1978, 150), who considered
compounds with selected coordination numbers at
the sulphur atoms.

SUM OF S-N BOND ORDERS

04.1—9   ON THE GEOMETRY AND THE BONDING RELA-
TIONSHIPS AT THE TWOFOLD COORDINATED
NITROGEN IN C-N-S AND S-N-S FRAGMENTS.

By V. Lamm and A. Gieren. Max-Planck-Institut
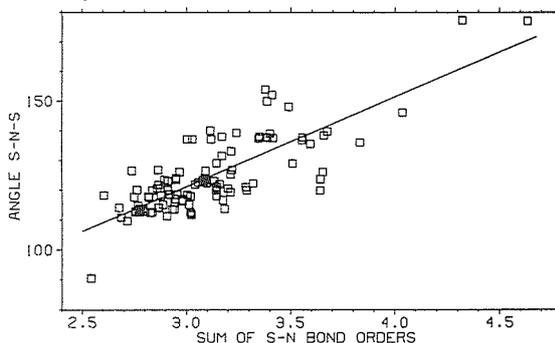f. Biochemie, Abteilung f. Strukturforschung I,
8033 Martinsried, FRG

For molecular fragments C-N-S or S-N-S ˎcon-
taining a twofold coordinated nitrogen. corre-
lations can be found between the two bond dis-
tances and the enclosed bond angle derived from
X-ray data. For both systems all coordination
numbers of nitrogen bound atoms were permitted
in these considerations.
The relationship between the two bond distances
(SN vs. CN) in the C-N-S fragment is shown in
Fig. 1. Due to the small variations of the bond
angles, the latter may be in a first approxima-
tion neglected. The regression line is well
defined by the 128 data points (k=-0.75) but is
unsuitable for an extrapolation beyond the

C-N BOND DISTANCE

04.1—10   ANGULAR RING DISTORTIONS IN BENZENE DERIVA-
TIVES: THE EFFECT OF THE NO$_2$ AND COOH SUBSTITUENTS

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Angular distortions in polysubstituted benzene rings
may be described, at least as a first approximation, by
superimposing separate contributions from each substi-
tuent. The effect of a substituent
may then be expressed by a set of
four 'angular substituent parame-
ters', Δα = α - 120°, Δβ = β - 120°,
Δγ = γ - 120°, Δδ = δ - 120°.
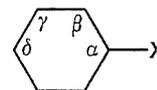
Angular parameters for several substituents, includ-
ing NO$_2$ and COOH, have been derived by regression from
large samples of polysubstituted benzene rings [Domeni-
cano & Murray-Rust, Tetrahedron Lett. 2283 (1979); Nor-
restam & Schepper, Acta Chem. Scand. A35, 91 (1981)].
We have recently shown, however, that deviations from
additivity occur when a π-donor is para to a π-acceptor,
due to cooperative interactions between substituents
[Colapietro et al., Z. Naturforsch. 37b, 1309 (1982)].
There are also indications that deviations from additiv-
ity occur with some ortho-disubstituted derivatives.
Accurate angular parameters must be derived, therefore,
either by direct measurement on monosubstituted deriva-
tives, or by regression from polysubstituted derivatives
with appropriate patterns of substitution.

The following benzene derivatives, containing only NO$_2$

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 San-severino, Acta Cryst. B36, 586 (1980).

Terephthalic acid: Triclinic, space group $P\bar{1}$, a = 5.027, b = 5.360, c = 7.382 Å, α = 115.72, β = 101.06, γ = 92.91°, Z = 1, D_c = 1.587 g cm^{-3}. Refined to R = 0.0550 using 630 counter intensities. Further refine-ment 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 & Mar-ciante, 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, β = 115.63°, Z = 16, D_0 = 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°, $\Delta\beta$ = -1.86°, $\Delta\gamma$ = 0.29°, $\Delta\delta$ = 0.45°;
$COOH$: $\Delta\alpha$ = 0.01°, $\Delta\beta$ = -0.24°, $\Delta\gamma$ = 0.01°, $\Delta\delta$ = 0.45°.

Inspection of the residuals shows that in most cases the additivity of angular distortions is respected with-in 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, proba-bly 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 struc-tures of 4-hydroxybiphenyl (hereafter, BIPHOH) that shed light on the problematic structure of the parent mole-cule.

One polymorph of BIPHOH is almost isostructural with the room-temperature form of biphenyl (and 4,4'-dihy-droxybiphenyl), but crystallizes in the non-centrosymmet-ric space group Pa with two full molecules in the asym-metric 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 $<L^{22}>$ about the long molecular axis is 72(6) deg^2. The 1:3 complex of BIPHOH with 4,4'-dinitrobiphenyl also con-tains nearly planar [ψ = 0.5(5) deg] BIPHOH molecules that have similar L^{22} values. These librational ampli-tudes are not much larger than those observed at room temperature for the 4,4'-dinitrobiphenyl molecules in the complex [$<L^{22}>$ = 34(4) deg^2; ψ = 37,37,37 deg], or for the well-ordered structures of 4,4'-dichlorobiphenyl [$<L^{22}>$ = 38(2) deg^2; ψ = 39,42 deg] or 4-biphenylcarbox-

ylic acid [$<L^{22}>$ = 50(5) deg^2; ψ =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 inver-sion symmetry (which is absent for the Pa modification of BIPHOH), but is rather a product of the overall crys-tal packing arrangement. Secondly, the wide distribu-tions associated with the atomic positions of the linear polyphenyls are not necessary results of the molecules' crystallizing with ψ=0 deg. Relatively narrow distribu-tions 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, Meinnel, Dworkin, Moussa & Zeyen (1980). Faraday Discuss. Chem. Soc., 7-18.

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

Compounds of composition $1RE_2O_3:2GeO_2$ show the largest structural variety of rare earth germanates known so far in the two-component systems RE_2O_3-GeO_2, RE:La...Lu. 1:2-germanates display 5 different structure types in-cluding 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; α=88.75, β=90.78,γ=95.83°) and $Ce_4[Ge_3O_{10}/GeO_4]$ (P1,Z=1,a_0=6.888, b_0=7.058,c_0=7.047 Å, α=116.11,β=91.35,γ=87,66°). 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 coor-dination. 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 ger-manates 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 $Ce_4^{4+}Ce_{10}^{3+}$ $[(GeO_4)_6(Ge_2O_7)_4(Ge_3O_{10})_2]$ 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.