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05. PHYSICAL PROPERTIES AND STRUCTURE

05.2-24 CRYSTAL AND ELECTRONIC STRUCTURE OF (μ-H)₃
(CO)₉H₃BOO. By Leh-Teh Hsiu, Dang-Tang Yang and Sheldon
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The title compound (I) has been prepared and characterized by
single-crystal X-ray diffraction as well as spectroscopic methods
(13C, 11B, and 1H NMR). The compound is a carbonyl boron
heptacarbonyl capped O₃ triangle as shown in the figure.

The electronic structure of I has
also been studied by using the
Fenene-Hall quantum chemical
approach with a fragment analysis
in terms of the metal cluster H₃(CO)₁₉⁺
and capped ligand BOD. The
calculation suggests that the apical bonding in 1 is electron rich and the π system acts as a lone electron donor and electron acceptor. A localized MO description with a sp-hybridized boron forms a dative bond to the metal triangle and the remaining p orbitals form multi-
centered π bonds to the O₃ group.

The BOD unit in I has
B=0.1.469(13)Å and C=0.1154(13)Å, while in H₃BOO (II) has B=0.1.454Å and C=0.1.313Å. The CO
stretching frequency is 2120 cm⁻¹ in I and 2140 cm⁻¹ in II. To explain this difference, nonparameterized Fenene-
Hall molecular orbital calculations are carried out on both I and II with a fragment analysis in terms of H₃(CO)₁₉
and CO for the former, H₃BO and CO for the latter. The calculation suggests that the back π bonding in 1 is
more significant, due to the predominant movement of the electron density of the main O₃B bonding orbitals to the
CO π antibonding orbitals.

05.2-26 A COMPARISON OF THE CRYSTAL AND MOLECULAR
STRUCTURES OF THREE POLYMORPHS OF NEMATOCIC 4,4’-
BIS-(ETHOXY)AZOBENZENE. By C. E. Pfluger, Dep. of
Chem., Syracuse University, Syracuse, N.Y., and R. D.
Oillard, and C. F. George, Laboratory for the Structure of
Matter, Naval Research Laboratory, Washington, D.C.,
USA.

The room temperature structures (12°C) of three crystal
polymorphs of the compound 4,4’-bis(ethoxy)-azobenzene (also called p,p’-azoxydiphenol), a compound exhibiting a nematic liquid crystalline phase from 137 to 168°C, as well as a low-temperature
structure of the triclinic polymorph, have been determined. These structures represent the initial
phase of a systematic variable temperature X-ray
crystallographic study of several members of a homologous series (4,4’-bis(ethoxy)-, 4,4’-bis(ethoxy)-
and 4,4’-bis(propoxy)-azoxybenzene) in an attempt to
obtain information regarding the intra- and
inter-molecular interactions which must account for
the liquid crystalline behavior of this series of
compounds. The isolation of three crystal polymorphs
at room temperature presents an opportunity to compare the intra- and inter-molecular interactions for
this nematic molecule in three different packing
arrangements. A comparison of the low- and room-
temperature structures has been useful in extracting
atomic thermal motion information from the somewhat
disordered crystal structure of the triclinic
polymorph.

05.2-27 THE EFFECT OF CRYSTAL STRUCTURE AND PHASE
STABILITY ON THE SUPERCONDUCTIVITY OF EQUATOINC
TERNARY PHOTIC COMPOUNDS. By C. F. Meisner, Los Alamos
National Laboratory, MST-5, Los Alamos, NM 87545, USA.

The equatomic ternary compounds M'X with M = Ti, V,
M₆, M₉ = Ru or Os, and X = P or As typically crystallize
at high temperatures in the TrzRuI-type hexagonal structure
(Fhex, M in 3(g), X in 3(f), and M in 3(c) and 1(b)) and exhibit superconductivity at temperatures as high as
13.3 K for Os₃B and CO for the former, H₃BO and CO for the latter.

The calculation suggests that the back π bonding in I is
more significant, due to the predominant movement of the
electron density of the main O₃B bonding orbitals to the
CO π antibonding orbitals.

The study by electron microscopy of virgin crystals (Franco and
Fernández-Ferrer,1986) obtained by evaporation from a water solutio-
shows two kind of crystals, which we have identified by X-ray
powder analysis; 45 relevant peaks of diagrams are indexed accord-
ing to the cell parameters of structure of ferroelectric phase of
TGS, and 41 with the cell parameters of switching fatigued struc-
ture.

The appearance of nematic phase of TGS in the virgin crys-
tals suggest the possibility to remove a crystal and refine:
the previous crystal structure, because switching fatigued crystals
show a lot of defects due to the aging process. The virgin pyroel-
etric phase has crystals with a size of this series of
compounds. The isolation of three crystal polymorphs
at room temperature presents an opportunity to compare the intra- and inter-molecular interactions for
this nematic molecule in three different packing
arrangements. A comparison of the low- and room-
temperature structures has been useful in extracting
atomic thermal motion information from the somewhat
disordered crystal structure of the triclinic
polymorph.