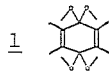**09.1-05**   THE ANTI,ANTI CONFORMATION OF
TETRAMETHOXY-TETRAMETHYL-1,4-CYCLOHEXADIENE.
   AN OVERRIDING OF THE ANOMERIC EFFECT.
By M.G.Ettlinger, J.Jaroszewski and L.Nørskov.
   Department of Organic Chemistry, University
   of Copenhagen, DK-2100 Copenhagen, DENMARK.

The title compound 1 has been studied by X-ray
diffraction analysis at 96 K.

1

The compound reveals some interesting conforma-
tional features. The methoxy groups adopt an
anti,anti conformation which is quite unusual
and opposed to the normal gauche,gauche form
dictated by the anomeric effect. The molecular
site symmetry is -1 and the geometry of the
acetal group is characterized by C(central)-O =
1.431(1)Å O-Me = 1.425(1)Å Me-O-C = 115.0(1)°
O-C-O = 99.0(1)° and Me-O-C-O = 180(1)°. The
extraordinarily small O-C-O angle is in accord
with ab initio calculations on dimethoxymethane
(Gorenstein&Kar JACS 99(1977)672) but our cen-
tral C-O bond lengths are significantly longer
than those calculated by Jeffrey et al. (JACS
100(1978)373). In search of the origin of the
anomeric effect force field calculations have
been employed. Thus the reason for the very
small O-C-O angle in the anti,anti conformation
is elucidated by these calculations.
   Another aspect of 1 is the presence of the
sterically hindered methyl groups on the double
bonds. The two groups are different in terms
of their rotation with respect to the double
bond. One has a hydrogen eclipsing the double
bond, the other has one perpendicular to it.
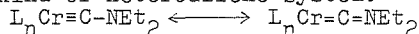

09.1-06   BONDING OF AMIDINE LIGANDS.
By N Cameron and M Kilner, University of Durham
England, M M Mahmoud*, and S C Wallwork,
University of Nottingham, England.

Amidino groups -N(R').C(R):NR' are isoelec-
tronic with both allyl and carboxylato groups;
so, like them, they may be expected to exhibit
a number of bonding modes when acting as
ligands to metal atoms. There is the possib-
ility of π attachment, with the plane of the
ligand perpendicular to the ligand-metal bond.
There is also the possibility of σ attachment
in a unidentate manner, using one nitrogen
atom, or in a bidentate or bridging manner,
using both nitrogen atoms. Further possibili-
ties are σ,π attachment involving σ bonding
from one nitrogen and π-bonding from the C=N
bond to the other nitrogen atom, or bidentate
or bridging attachment involving one nitrogen
together with some other atom of the ligand.
For bidentate or bridging attachment, there is
also the interesting question of the extent of
electron delocalisation within the N-C=N
system. A number of complexes containing
amidino groups are therefore being examined
crystallographically to establish the range
of bonding modes encountered in practice and
to examine the detailed geometry of those that
do occur. The present paper describes two
cases of σ,σ bidentate bonding to palladium,
one involving the two nitrogen atoms and one
involving one nitrogen atom and the ortho
carbon atom of a phenyl ring attached to the
other nitrogen atom.

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Al-Mustansiriyah University, Bagdad, Iraq.

09.1-07   AMINOCARBYNE COMPLEXES OF CHROMIUM:
STRUCTURES AND BONDING. By U.Schubert, D.Neu-
gebauer, K.Ackermann, Anorganisch-chemisches
Institut der Technischen Universität München,
Garching; P.Hofmann and B.E.R.Schilling,
Institut für Organische Chemie I, Universität
Erlangen, W-Germany.

Structure determinations of the aminocarbyne
complexes [trans-L(CO)$_4$CrCNEt$_2$]BF$_4$ (L=PPh$_3$
and CO), mer-Br(PPh$_3$)(^{4}CO)$_3$Cr^{2}CNEt$_2$ and
trans-L(CO)$_4$CrCNEt$_2$^{3}(L=Br ^{3}[Fischer, Huttner,
Kleine and Frank, ^{2}Angew.Chem.Int.Ed.(1975)
14,760], SnPh$_3$ and SePh) have been performed
in order to obtain information about the
influence of the varying metal complex moiety
on the bonding parameters of the carbyne li-
gand. Extended-Hückel-MO calculations at
suitable models and the analysis of fragment
orbital interactions serve the discussion of
bonding. In each complex the amino group is
conjugated with the Cr-C(carbyne) bond, form-
ing a kind of heteroallene system.
   $$L_nCr\equiv C-NEt_2 \longleftrightarrow L_nCr=C=NEt_2$$
The degree of conjugation can be influenced
by the σ- and π-donor abilities of the ligand
trans to the carbyne group and can be
followed by the Cr-C and C-N bond lengths.
In Br(CO)$_4$CrCNEt$_2$ the highest Cr-C(carbyne)
bond order is found (Cr-C 1.72(1), C-N 1.29(1)
Å), in [(CO)$_5$CrCNEt$_2$]BF$_4$ the lowest one
(Cr-C 1.80(1), C-N 1.26(1) Å). For cis
ligands other influences have to be discussed,
too.

09.1-08   THE POLYMETHINIC STATE— A STRUCTURAL
PRINCIPLE OF UNSATURATED ORGANIC COMPOUNDS.
By S.Kulpe, Central Institute of Physical
Chemistry, Academy of Sciences of the German
Democratic Republic, DDR-1199 Berlin.

Most coloured organic compounds contain poly=
methinic fragments of the general formula
$$X-(Y)_{N-2}-X' \qquad \frac{(N+1)\pi}{} $$
N = 2,3,4...
X,X',Y=atoms of the groups IV,
V or VI of the periodic table
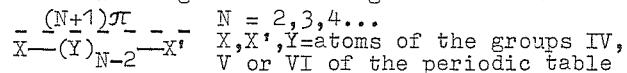
odd N from 3 upwards corresponds to polymethi=
nic dyes, even N from 2 upwards corresponds
to polymethinic radicals (Dähne;Kulpe: Abh.
Akad.Wiss.DDR (1977)N8,1-128).The ideal poly=
methinic state is characterized by: high reso=
nance energy; maximum equalisation of π-bond
orders; strongly alternating π-electron den=
sity distribution along the polymethinic chain
in the ground state. Polymethines show e.g.
deep colour, high optical polarisability,
preferentially nucleophilic and electrophilic
substitution reactions. The polymethinic state
besides the aromatic and polyenic state is a
basic structural element in unsaturated orga=
nic compounds. Many structures may be consi=
dered as being composed from polymethinic,
aromatic and polyenic fragments(Dähne;Leupold:
Angew.Chem.(1966)78,1029;Fabian;Tröger-Naake:
J.prakt.Chem.(1976)318,801 and Dähne;Kulpe:
J.prakt.Chem.(1978)320,395). Where the number
of π-electrons in compounds of comparable
size is identical, compounds in the polymethi=
nic state will always be the deepest in colour,
that is they combine a maximum transition pro=
bability with a relatively low transition
energy. There exists a quantum chemical model
for the ideal polymethinic state(Fabian;Hart=

mann:J.Signal-AM.(1974)$\underline{2}$,457 and J.Molec.
Structure (1975)$\underline{27}$,67 and Theoret.Chim.Acta
(1975)$\underline{36}$,351) based on MO-theory. The polyme=
thinic electron system corresponds to a defin=
ed spatial configuration of the molecules and
a special intermolecular arrangement. Results
of X-ray diffraction have contributed essen=
tially to the general understanding and to the
development of the theory. Significantly geo=
metrical features of the polymethinic state
are:equalisation of bond lengths and alterna=
tion of valence angles (Kulpe;Zedler;Dähne;
Nolte: J.prakt.Chem.(1973)$\underline{315}$,865); special
intermolecular aggregation(Kulpe;Dähne;Ziemer;
Schulz:Photogr.Sci.Eng.(1976)$\underline{20}$,205),long bond
lengths between $C sp^2$ atoms in coupled polyme=
thines(Kulpe;Dähne:Acta Cryst.(1978)$\underline{B34}$,3616).
In the last case canonic structures with the
same sign of charge at neighbouring atoms are
preferred as opposed to Pauling's rule
(Pauling:Proc.nat.Acad.Sci.USA(1932)$\underline{18}$,498).
Special behaviour of the carbonyl group can
be explained on the basis of the polymethine
concept(Kulpe:Z.Chem.(1980)$\underline{20}$,377 and Angew.
Chem.in press). In photochromic azomethine
imine-1.3-dipoles heteroatom polymethinic
fragments are present causing strong intermo=
lecular C-H···O hydrogen bonds (Kulpe;Seidel:
Z.phys.Chem.in press). Nearly ideal polymethi-
nic compounds are e.g. open chained cyanines
and oxonols and coupled polymethines like sub=
stituted hydroxybenzoquinones, aminobenzoqui=
nones, oxalates and oxamates (Fabian:J.prakt.
Chem.(1978)$\underline{320}$,316). Typical polymethine
radicals with branched polymethinic fragments
are Wurster's coloured salts (cf.1.ref.). NMR
spectroscopy provides further experimental
verification of the polymethinic electron
system (Radeglia:J.prakt.Chem.(1974)$\underline{316}$,344).

09.2-01 THE CRYSTAL AND MOLECULAR STRUCTURE OF
3'-FLUOROBIPHENYL-4-CARBOXYLIC ACID. By A. Rawas and
H.H. Sutherland, Physics Department, University of Hull,
Hull, England.

3'-Fluorobiphenyl-4-carboxylic acid, $C_{13}H_9O_2F$, is mono-
clinic, space group $P2_1/c$, with a = 3.92(1), b = 8.04(1),
c = 32.50(2)Å, β = 101.6(1), Z = 4, D_m = 1.42,
D_c = 1.43 Mg m^{-3}. The structure was solved by Patterson
synthesis with CuKα x-ray data measured by densitometer
and visually from equi inclination Weissenberg photo-
graphs. It was refined anisotropically by block
diagonal least squares to R = 0.08 for 895 reflexions.
The average C-C bond in the two phenyl rings is 1.390Å.
The molecule is non planar; the two phenyl rings are
rotated about the phenyl-phenyl bond by 36.3° and the
acid group is rotated about its C-C bond by 3.6°. There
is also distortion in the bond angle around C(3) with
the internal angle of 124.5(1.2)° ; the C-F bond is
1.363(13)Å and makes an angle of 2° with the phenyl
plane.

Dimers formed from the molecules by an O-H...O bond
of 2.623(15)Å, pack in a herring bone arrangement with
the fluorine atoms lying in sheets parallel to (001).

09.2-02 THE CRYSTAL AND MOLECULAR STRUCTURES OF
SOME TERTIARY AMINE OXIDES.
E. Maia & S. Pérez. Centre de Recherches sur les Macro-
molécules Végétales (C.N.R.S.) Grenoble, France.

Recent investigations came to focus on tertiary
amine oxides which look most promising for their cellu-
lose disolving power. To elucidate some of their struc-
tural characteristics, along with their possible mode of
interactions with cellulose chains, a crystallographic
investigation has been undertaken. Most attention has
been devoted to N-methylmorpholine N-oxide (MMNO) :
($C_5 H_{11} N O_2$) .
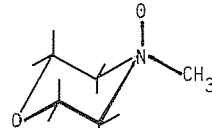
- Anhydrous MMNO (MP=172°C) is monoclinic $P2_1/m$,
(a = 9.886(5), b = 6.621(5), c = 5.112(4), β = 111.54(10)
Z = 2). The structure has been refined to R=0.047. The
molecule is found to be in a perfect chair conformation
and the N → O bond to be axially oriented with respect
to the ring.

-MMNO, H_2O (MP=73°C) is monoclinic $P2_1/c$ (a = 25.481
(9), b = 6.040(5), c = 9.186(6), β = 99.88(10) , Z = 8.
The structure has been refined to R = 0.042. Within the
crystal, the water molecules are structured into a poly-
mer-like fashion by the MMNO molecules through an
extensive hydrogen bonding scheme. There exists a dis-
tinct segregation between the hydrophobic and the hydro-
philic parts of the structure.

-MMNO, 2.5 H_2O (MP=36°C) is monoclinic $P2_1/c$,
a = 12.803(6), b = 6.500(4), c = 21.913(8),β=109.99(10)
(Z = 8). The structure has been refined to R = 0.042.
An intricate network of 10 different hydrogen bonds
holds the molecules in the crystal.

-MMNO : 1,2-trans-cyclohexanediol complex is monocli-
nic, $P2_1/c$, (a = 6.137(3), b = 10.153(4), c = 21.015(6)
β = 94.33(10), Z = 4). The structure has been refined
to R = 0.042. The geometry and conformation of MMNO are
the same as those found in the other structures. The
1,2-trans-cyclohexanediol molecule is in a chair confor-
mation and the hydroxylic oxygen atoms are in a diequa-
torial arrangement. The N → O structuring site of MMNO
links through bifurcated hydrogen bonds contiguous
1,2-trans-cyclohexanediol molecules oriented into a
polymer-like fashion.