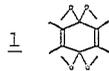


09.1-05 THE ANTI, ANTI CONFORMATION OF TETRAMETHOXY-TETRAMETHYL-1,4-CYCLOHEXADIENE. AN OVERRIDING OF THE ANOMERIC EFFECT.

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.



The compound reveals some interesting conformational 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 $\bar{1}$ 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 central 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.

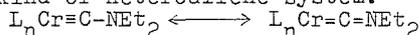
By N Cameron and M Kilner, University of Durham England, M M Mahmoud*, and S C Wallwork, University of Nottingham, England.

Amidino groups $-N(R')C(R):NR'$ are isoelectronic 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 possibility 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 possibilities 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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09.1-07 AMINOCARBENE COMPLEXES OF CHROMIUM: STRUCTURES AND BONDING. By U.Schubert, D.Neugebauer, 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.

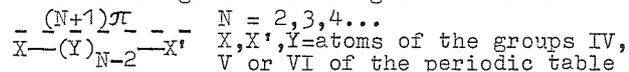
Structure determinations of the aminocarbene complexes $[trans-L(CO)_4CrCNET_2]BF_4$ (L=PPh₃ and CO), mer-Br(PPh₃)₃(CO)₃CrCNET₂ and trans-L(CO)₄CrCNET₂ (L=Br) [Fischer, Huttner, Kleine and Frank, Angew.Chem.Int.Ed.(1975) 14,760], SnPh₃ and SePh) have been performed in order to obtain information about the influence of the varying metal complex moiety on the bonding parameters of the carbene ligand. 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(carbene) bond, forming a kind of heteroallene system.



The degree of conjugation can be influenced by the σ - and π -donor abilities of the ligand trans to the carbene group and can be followed by the Cr-C and C-N bond lengths. In Br(CO)₄CrCNET₂ the highest Cr-C(carbene) bond order is found (Cr-C 1.72(1), C-N 1.29(1) Å), in [(CO)₅CrCNET₂]BF₄ the lowest one (Cr-C 1.80(1), C-N 1.26⁴(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 polymethinic fragments of the general formula



odd N from 3 upwards corresponds to polymethinic dyes, even N from 2 upwards corresponds to polymethinic radicals (Dähne; Kulpe: Abh. Akad. Wiss. DDR (1977) NS, 1-128). The ideal polymethinic state is characterized by: high resonance energy; maximum equalisation of π -bond orders; strongly alternating π -electron density 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 organic compounds. Many structures may be considered 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 polymethinic state will always be the deepest in colour, that is they combine a maximum transition probability with a relatively low transition energy. There exists a quantum chemical model for the ideal polymethinic state (Fabian; Hart-