

group rotations and PPh₃ gearing motion was inferred: (+C) \leftrightarrow (+A) \leftrightarrow [(+B) or (+B)] \leftrightarrow (-A) \leftrightarrow (-C) \leftrightarrow etc.

The above analysis of a molecule with many (>3) torsional degrees of freedom is based on specially developed concepts and methods. First, the conformation of each PPh₃-group and of each phenyl group is described by a single torsion angle, thus disregarding deviations from local C_{3v}- or C_{2v}-symmetry, respectively. Second, the symmetry of the resulting 8-dimensional conformational space is taken into account. Symmetry implies - among other things - a periodic structure of this space due to the cyclic nature of torsional coordinates. (Murray-Rust, Bürgi and Dunitz, Acta Cryst. A35 (1979) 703). This structure may be utilized by analyzing several, adjacent asymmetric units together (i.e. a data set containing an integer multiple of the original 62 data points) and by transforming torsion angles into appropriate sine and cosine values. Regions in conformational space which are densely populated with data points, were located using Ward's method of cluster analysis (Ward, J. Am. Stat. Ass. 58 (1963) 236) as implemented in SAS-procedure CLUSTER (SAS User's Guide: Statistics, SAS Institute Inc. (1982) Cary NC, USA). The clustering process treats every data point as a cluster, then joins neighboring clusters into new ones until all data points form a single cluster. For present purposes the process is intercepted, however: the final set of clusters is obtained with the following two criteria: (1) the set must conform to the symmetry of conformational space, and (2) a statistical clustering criterion must be a maximum.

04.3-7 INTERACTIONS BETWEEN DIAZONIUM GROUPS AND NUCLEOPHILIC CENTRES ATTACHED TO THE PERI POSITIONS OF NAPHTHALENOID RING SYSTEMS. IMPLICATIONS FOR THE PREFERRED DIRECTION OF NUCLEOPHILIC ATTACK ON N,N TRIPLE BONDS. By John D. Wallis and Jack D. Dunitz Organic Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zürich, CH-8092 Zürich, Switzerland.

The crystal structures of the BF₄⁻ salts of the 8-quinolinediazonium-1-oxide (1), 8-dimethylamino-naphthalene-1-diazonium (2) and 8-nitronaphthalene-1-diazonium (3) cations have been measured at low temperatures (95 - 150 K, R ≤ 0.04). All three structures show an interaction between the α-N of the diazonium group and a nucleophilic centre (O for 1 and 3, N for 2). Distances between these interacting atoms lie in the range 2.44 - 2.54 Å, i.e. they are less than the sum of the appropriate van der Waals radii. The diazonium groups are bent (C-N_α≡N_β angles of 167° - 171°) so that N_α deviates from the C...N_β vector towards the nucleophilic centre.

In 1 and 2 the substituents are not splayed apart; instead the bond to the diazonium group bends outwards and the one to the nucleophilic centre bends inwards by a similar amount (1 by 2°, 2 by 3-4°). This helps to increase the O...N_α≡N_β and N...N_α≡N_β angles to 104° and 106° from near 90° in the undistorted molecule. Since in 1 there is no steric hindrance to distortion in the opposite direction the preferred direction of nucleophilic attack on the -N≡N bond makes an angle of at least 104° to the bond axis.

04.3-8 UNEXPECTED REACTIONS WITH 1,3-DIAZABUTA-1,3-DIENES. By A. Gieren, T. Hubner, C.-P. Kaerlein, G. Weber, H. Betz and K. Burger*, Max-Planck-Institut für Biochemie, Abt.f.Strukturforschung I, Martinsried, BRD; *Institut für Organische Chemie der TU, München, BRD.

In the case of reactions of very polar dienes with dienophiles in contrast to conventional [4+2] cycloadditions following the concerted Diels-Alder scheme, more step processes are favoured as we could demonstrate with 2-phenyl-4,4-bis(trifluoromethyl)-1-(aryl)-1,3-diazabuta-1,3-dienes (1) as a model. The adducts 6-10 of the reactions of 1 (1a, 1b) with the nitriles 2-4 and the α,β-unsaturated ketone (5) have been characterized by X-ray structure analyses and new reaction patterns could be deduced.

The reactions of 1 with the nitriles 2-4 and the α,β-unsaturated ketone (5) follow different more step mechanisms. In the case of reaction with 2 a reorganisation of the diene skeleton occurs during the reaction. In the reaction with 3 a five membered ring system (7) is formed, which formally can be described as an isonitrile adduct. In the case of the reaction with 4, the [4+2] adduct formed reacts further in a very complex manner with a second molecule of the heterodiene under elimination of HF, yielding 8. With respect to the formation of the isomers 9 and 10 a reaction sequence diene metathesis/intramolecular ene reaction and diene metathesis/electrocyclic ring closure is proposed, respectively.

