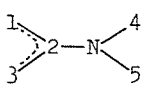
04.3-01 INTERACTIONS OF NUCLEOPHILES WITH QUATERNARY PHOSPHONIUM CENTRES. STRUCTURE OF BENZYLTRIPHENYLPHOSPHONIUM IODIDE AND STRUCTURAL CORRELATION OF RELATED SYSTEMS.
By S.J. Archer, T.A. Modro and L.R. Nassimbeni, School of Chemical Sciences, University of Cape Town, Rondebosch 7700, Republic of South Africa.

The crystal and molecular structure of benzyltriphenylphosphonium iodide was determined. This salt crystallises in space group $P2_1/c$, with a = 9.692(5), b = 21.58(1), c = 11.211(6)Å; $\beta = 107.2(2)^\circ$; Z = 4. The structure was refined to a final R value of 0.052. This structure, together with all structures of the quaternary phosphonium salts $R_4P^+X^-$, available through the CCDC file, was subject to the correlation treatment, introduced by Dunitz et al. Exclusive "face" orientation of X^- with respect to the tetrahedral phosphonium centre was demonstrated. Analysis of the secondary interactions of X^- with the organic cation indicated that the systems studied yield better models for ylid formation (α-hydrogen abstraction) than models for nucleophilic attack at the P^{IV} atom.

04.3-02 ROTATION AROUND THE $C(sp^2)$-$N(sp^3)$ BOND AND NITROGEN PYRAMIDALIZATION. By G. Gilli and V. Bertolasi, Centro di Strutturistica Diffrattometrica, University of Ferrara, Ferrara, Italy.

Results of crystal structure analyses of molecules containing the $C(sp^2)$-$N(sp^3)$ group are surveyed. They include 19 anilines, 18 amides, 11 amidines and 12 enamines when only N-dialkyl derivatives are taken into account.



The out-of-plane deformation of the group is described in terms of the torsion angles w1=1-2-N-4, w2=3-2-N-5 and w4=1-2-N-5 and of their linear combinations, i.e. twisting (τ) and out-of-plane bending (χ_C,χ_N) coordinates (Winkler & Dunitz, J.Mol.Biol.,169,1971).

The results can be summarized as follows:
- Carbon has a much greater resistance to bending than nitrogen, so that χ_C can be usually neglected;
- Amides show the highest resistance to twisting ($\tau < 13^\circ$) and bending ($\chi_N < 22^\circ$);
- All other compounds are much more flexible and values as high as 87° and 55° can be observed for τ and χ_N respectively;
- Two different ways of nitrogen pyramidalization can be identified, one through simple bending at τ nearly zero, the other through bending and concomitant twisting;
- The distribution of the experimental points in the χ_N vs. τ plot is consistent with a potential energy surface of the type

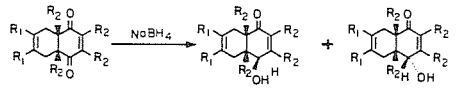
$$V(T,X)=(CTIB+IB)(1-\cos T)/2 + QP(1+\cos T)X^2/2 + IB(1-\cos T)(\cos 3X-1)/4$$

where $X=\chi_N$, $T=2\tau$, CTIB=cis-trans isomerization barrier, IB=nitrogen inversion barrier and QP=quadratic term for nitrogen out-of-plane vibration;
- This potential function neglects the asymmetry of the non-bonded interactions and it can be shown that these are responsible for the uneven distribution of points in the four quadrants of the (χ_N,τ) plot;
- Finally the C2-N bond distances are found to range from 1.31 to 1.45 Å and to depend on both bending and twisting coordinates. A smooth curve is obtained when the distances are plotted against the independent variable (|w1| + |w2|).

The present results confirm and extend previous findings on the characteristics of the $C(sp^2)$-N(piperidyl) bond (Gilli & Bertolasi, J.Amer.Chem.Soc.,101,7704,1979), on the deformation of the amide group in medium-ring lactams (Dunitz & Winkler, Acta Cryst.,B31, 251,1975) and on the geometry of crystalline enamines (Brown, Damm, Dunitz, Eschenmoser, Hobi & Kratky, Helv.Chim.Acta,61,3108,1978).

04.4-01 SOLID STATE PHOTOCHEMISTRY OF NAPHTHOQUINONES. By J.R. Scheffer, A.J. Secco and J. Trotter, Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Y6.

The solid state photochemistry of cis-4a,5,8,8a-tetrahydro-1,4-naphthoquinone derivatives is investigated and the results are correlated with X-ray crystal structure data. Despite the identical conformations of the molecules, three different types of reactivity are observed: intramolecular hydrogen abstraction, topochemically controlled bimolecular 2+2 ene-dione photocycloaddition, and internal oxetane formation. The bimolecular photoaddition occurs only when adjacent molecules in the crystal are favourably oriented. The intramolecular hydrogen abstractions are facile in the solid state due to favourable geometric and distance factors, and to the fact that the biradical intermediates produced by abstraction have favourable conformations for direct collapse to stable products. The oxetane formation occurs only for one molecule in which the structure is unfavourable for the other processes. The close similarity between solid and solution state results suggests similar intramolecular processes in solution



The corresponding naphthoquin-4-ols give rise to two types of photoproduct in the solid state, resulting from control of molecular conformation by the configuration of the OH substituent at position 4. The solution photoproducts arise from a higher-energy eclipsed conformation.