Non-centrosymmetry in Organic Crystals: a Study of Molecular Conformation in some Substituted Tolans

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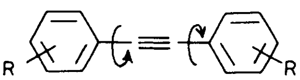
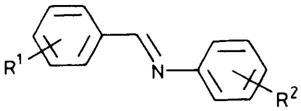
Unsymmetrically substituted tolans with moderate dipole moments are likely to adopt non-planar, chiral conformations in the solid state and non-centrosymmetric space groups, rendering them useful for second harmonic generation applications.

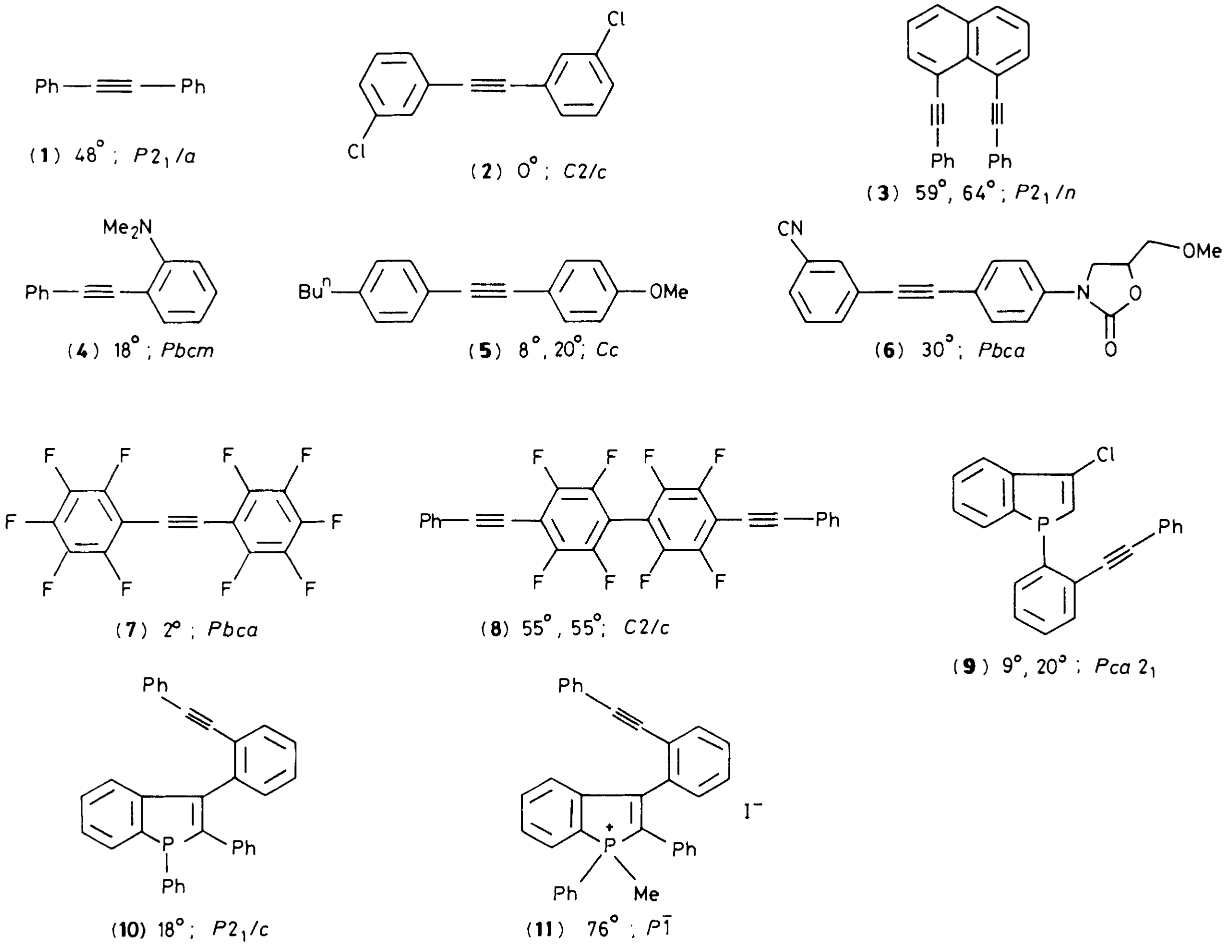
It has been well recognised that the systematic design of a new material for second harmonic generation (S.H.G.) may be conceptually divided into two steps: 'molecular engineering' wherein the electronic properties of the molecule are optimised and 'crystal engineering' wherein crystallisation in a non-centrosymmetric space group is achieved.[1] However, the main problem with this strategy is that these two steps are not generally independent of each other. For instance, a compound whose molecular structure has been optimised for



(A)



(B)



Scheme 1: compounds in this study with pertinent crystallographic details. (**5**) and (**9**) have two molecules in the asymmetric unit. The angles shown are between the best planes of the two six-membered rings flanking the triple bond.

S.H.G. by including a delocalised π-system may tend towards centrosymmetry because of the importance of dipole–dipole forces in crystal stabilisation. This study was prompted by the recent report of Kurihara *et al.*, that 4-methoxy-4′-nitrotolan (MNT) exhibits a highly efficient S.H.G.[2]

The aim of this work was to examine the generality of the tolan skeleton for S.H.G. applications. Our approach uses the Cambridge Structural Database.[3] A connectivity search of the Ar–C≡C–Ar fragment, where Ar is any (substituted) phenyl ring gave 66 hits from the 1985 version of the Database. Eighteen compounds were left after removing the organometallic complexes of tolan. Seven cyclic acetylenes were also excluded. We focussed our attention upon compounds (**1**)—(**11**) which remained.† Scheme 1 gives the space groups for compounds (**1**)—(**11**) and also the angles between the best planes of the two six-membered rings which flank the triple bond in these compounds.

These interplanar angles vary over a wide range, usually increasing with the electronegativity difference of the substituents on the two phenyl rings. Values close to 0° are obtained only for the symmetrical compounds (**2**) and (**7**). For (**2**), molecular planarity is a consequence of crystallographic symmetry. Since free rotation about the C–C≡ single bond is possible in all the compounds except (**3**), we conclude that the large interplanar angles observed are the result of crystal packing forces. As is well known, the crystalline environment can effect such torsional changes easily.[4]

The molecular chirality which results from a non zero interplanar angle for such molecules is a necessary though not a sufficient condition for non-centrosymmetry. If molecules of only one handedness are present, crystallisation in an enantiomorphous and therefore non-centrosymmetric space group must follow, but *RS* pairs may crystallise in both non-centrosymmetric and centrosymmetric space groups. We feel that the presence of a –C≡C– bond in the molecule confers a distinct advantage in the adoption of a non-planar, chiral conformation since resonance between the aromatic rings and the triple bond is unaffected by single bond rotation (A). In contrast, compounds such as the *N*-benzylideneanilines (B), while displaying a variety of polymorphs, invariably adopt at least one in which the interplanar angle is close to or equal to zero.[5] Obviously, this is because there is a driving force for both phenyl rings to be conjugated with the same π-bond.

All this suggests that non zero interplanar angles are expected to be the rule rather than the exception for unsymmetrically substituted tolans. A closer inspection of compounds (**1**)—(**11**) reveals that non-centrosymmetry may

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† Database REFCODES for the compounds: (**1**) DPHACT, (**2**) DMCPAY, (**3**) PEYNAP, (**4**) CENGIL, (**5**) MXTBAC, (**6**) BOGFAE, (**7**) PFDPAY, (**8**) PEYOFB, (**9**) CETHOY, (**10**) PEYPIN, (**11**) MPEPIN

further result only if there is a moderate electronegativity difference between substituent groups on the two rings, as in (**5**) and (**9**). A similar view was expressed by Kurihara *et al.*, with regard to MNT.[2] We note further that if MNT is added to the list of eleven compounds in Scheme 1, the percentage of non-centrosymmetric crystals is 25% which is nearly equal to the statistical value when taken over all reported structures in the Database.

While symmetrical molecules with zero dipole moments such as (**1**), (**2**), (**7**), and (**8**) are likely to tend towards centrosymmetry for purely crystallographic reasons, it is possible that the dipole moments of (**4**) and (**6**) are high enough for 'centrosymmetric directing' dipole–dipole interactions to become important. An intermediate value of the dipole moment appears to be therefore optimal for non-centrosymmetry.

We conclude that the presence of the –C≡C– linkage in tolan derivatives is important in ensuring non-planar, chiral molecular conformations which may be expected to pack in non-centrosymmetric space groups if the molecular dipole moments have intermediate values.

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