

Synthesis & crystallographic, spectroscopic and computational characterization of O-R substituents effects on the torsional angle of 3,3',4,4' substituted biphenyls

N. Vadra,¹ L. D. Slep,¹ V. E. Manzano,¹ E. B. Halac,² R. F. Baggio,² S. A. Suarez,¹ and Fabio D. Cukiernik.¹

¹INQUIMAE, CONICET and Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón II – Ciudad Universitaria - Núñez (C1428EHA), CABA, Argentina,

²Gerencia de Investigación y Aplicaciones, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina.

vadra@qi.fcen.uba.ar

In this work we synthesize, characterize and study by single crystal & powder X-ray diffraction, Raman scattering and quantum mechanics calculations, the structure of a series of biphenyls substituted in positions 3,3',4,4' - with a variety of R- groups connected to the biphenyl core through oxygen atoms (R: methyl, acetyl, hexyl).[1,2] The six member series split into two groups with striking differences in molecular conformation as well as in melting points (viz., in the solid state three members are strictly planar and present significantly lower m.p., while the remaining three are highly twisted, with larger m.p.). Thus, the aim of the work is to understand if any of the intervening molecular fragments exerts any decisive influence on the molecular planarity as well as on the thermal stability of the compounds.

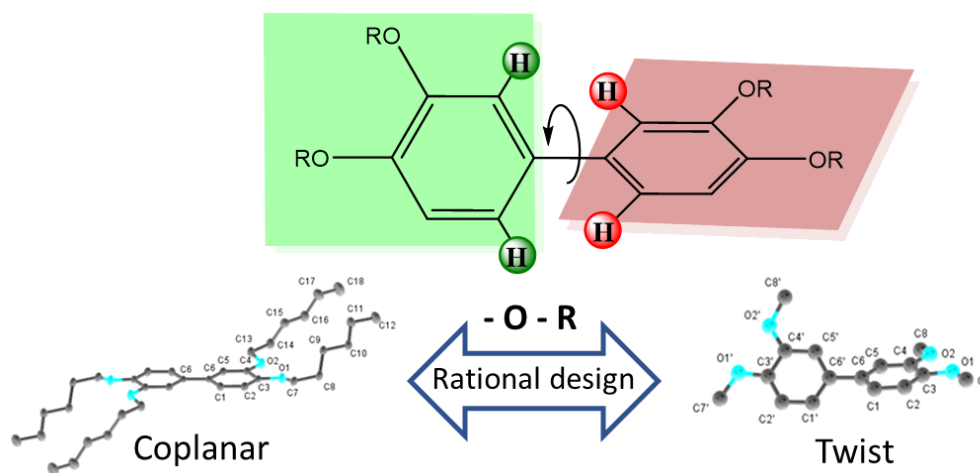


Figure 1. Design of biphenyls with different molecular conformation, based on the selection of the OR used

The molecular conformation, particularly the torsion angle between aromatic rings has been extensively studied both in the solid as well as in the liquid state. The results show that the three compounds appearing as rigorously planar in the solid (as assessed by single crystal X-ray Diffraction) present instead a twisted conformation in the melt (as disclosed by Raman experiments and/or quantum mechanics calculations). The solid vs melt issue strongly suggests that the reasons are to be found in the packing restraints, though it is not easy to find a straightforward explanation: in some cases (as those with the shorter substitution chains) the combined non-bonded interactions can be specifically pointed out as responsible for the effects, while in some others (as in the longer ones), they can be more subtle and diffuse, not directly ascribable to specific interactions.[2] Finally, a “rule of thumb” is suggested for the design of biphenyls with different molecular conformation, based on the selection of the OR used.[2,3]

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[3] Grineva, O. V. (2009). *J. Struct. Chem.* **50**, 727.

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