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The effect of β-particles on the crystallization of 1,1′-binaphthyl and 4,4′-dimethylchalcone

Rodney Sullivan,[a] Nicie Conley,[b] Robert N. Compton[a,b] and Richard M. Pagni*[b]

[a] *Department of Physics, University of Tennessee, Knoxville, TN 37996-1600, USA*
[b] *Department of Chemistry, University of Tennessee, Knoxville, TN 37996-1600, USA. E-mail: pagni@novell.chem.utk.edu*

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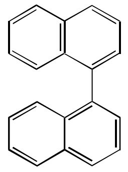
β-Particles affect the crystallization of 1,1′-binaphthyl from the molten state and 4,4′-dimethylchalcone from ethyl acetate by providing a heat source and thus convection currents in the crystallising media.

The asymmetric synthesis of crystals is a topic of current interest. The crystallization of sodium chlorate, an achiral ionic compound crystallising in the chiral $P2_13$ space group, has played a pivotal role in these studies.[1] In the absence of any perturbation, crystallization from water yields a random distribution of (+) and (–) crystals.[2] If the solution is stirred during crystallization, however, a given experiment will yield mostly (+) or (–) crystals.[3] There is also no correlation between the direction of stirring and the chirality of the crystals. If enough crystallizations are carried out under stirring, a random distribution of (+) and (–) crystals is obtained in total. The phenomenon is not unique to sodium chlorate. Recent work has shown that stirring has a similar effect on the crystallization of chiral 1,1′-binaphthyl **1** from its melt at 150 °C[4,5] and achiral 4,4′-dimethylchalcone **2** from ethyl acetate at room temperature.[6] Both compounds crystallise in chiral space groups.



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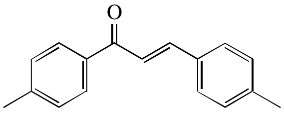

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When evaporating aqueous sodium chlorate is subjected to very energetic β-particles, which are predominantly left-handed, from a strontium-90 source, the resulting crystals have an enantiomeric excess of 33% in one set of experiments and 42% in a second set, with the (+) crystals predominating.[7] When the solution is subjected to positrons, which are predominantly right-handed, from a sodium-22 source, the resulting crystals are mostly (–), with an *ee* = 55%. There is thus a correlation between the chirality of the crystals and the impinging elementary particles. The origin of this interesting observation is unknown.

To see if the phenomenon described above is general, the crystallization of **1** and **2** while being exposed to beta particles was examined. The results of these experiments are described herein.

Vacuum sublimed **1** was placed in a small glass dish and heated to 180 °C and kept there for 20 min while being exposed to β-particles (^{90}Sr source, 26.970 mrad h^{-1} at 0.35 m). At this temperature, the enantiomers of **1** in the melt interconvert rapidly. The liquid was cooled to 150 °C under β-radiation and kept there until crystallization was complete. Any enantiomeric excess obtained during the crystallization process is retained in the crystal since interconversion of the enantiomers does not occur. After reaching room temperature, the crystals were dissolved in benzene and the enantiomeric excess was determined from the optical rotation measurement. Interconversion of the enantiomers in solution is slow at room temperature.[8] An identical set of runs was carried out but without exposure of **1** to β-particles.

On the other hand, **2** was crystallised from ethyl acetate with and without exposure to β-particles. The resulting crystalline **2** was initially brominated with bromine vapour, but in our hands a 2:1 ratio of *erythro* and *threo* dibromides was obtained. Instead **2** was brominated as a slurry in aqueous pyridinium perbromide where only *erythro* dibromide **3** from *anti* addition was formed.[9] This enabled the chirality of crystalline **2** to be transferred to molecular **3**, whose optical rotations were measured in methylene chloride.

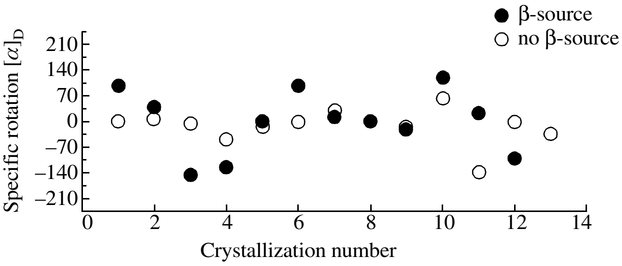

Figure 1 The effects of β-radiation on binaphthyl.

For compound **1**, 12 crystallizations under the β-particle source afforded an average enantiomeric excess of –2.7±10.3%, while the control 13 unstirred crystallizations afforded an average enantiomeric excess of –5.1±5.3%. The two sets of experiments thus yield enantiomeric excesses very close to zero, as expected for the random generation of (+) and (–) crystals. The greater standard deviation of the mean of 10.3% for the β-particle experiments as compared to 5.3% for the control unstirred experiments reflects the greater spread of enantiomeric excesses observed under the β-particle source. This is most easily seen in the scattergram above where the specific rotation found for a given crystallization is plotted against crystallization number. Note that in the scattergram experiments 8 and 9 yielded virtually identical results for the control and β-particle-induced crystallizations, and experiment 13 only has a control crystallization. Crystallizations under the β-particle source frequently yielded rotations larger than those observed for the control experiments.

For dimethylchalcone **2**, 28 crystallizations in the presence of β-particles afforded an average specific rotation of –10.1±22.8° while 12 control unstirred crystallizations yielded 0.0±13.9°. These specific rotations correspond to enantiomeric excesses of –6.0±13.7% and 0.0±8.3%, respectively.[10] As with **1**, both sets of crystallizations afford a random distribution of (+) and (–) crystals. The spread of enantiomeric excesses under the β-source is larger than for the controls, similar to what was observed for **1**.

Unlike what was seen for the crystallization of sodium chlorate under β-radiation, neither **1** nor **2** afforded an enantiomeric excess of crystals. Thus, β-particles do not affect the enantiomeric excess of primary nucleation of the two organic compounds when averaged over many crystallizations. β-Particles do have a big effect on the crystallizations in another way. Both **1** and **2** occasionally yielded crystallizations with large enantiomeric excesses, similar to that observed both with sample stirring.[4–6] β-Particles are very energetic. When they impinge on the crystallising medium, a complex chemistry is initiated and heat is dumped into the medium. Convection currents are created in the liquid which facilitates secondary nucleation, similar to what is observed with stirring.[11] Finally, these results have relevance to our previous studies of β-radiolysis of sodium chlorate solutions.[7] Thermal stirring of the solution by the slowing down of β-particles is surely occurring and can act to propagate any initial chiral bias initiated by the β-particles.

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