

Synthesis and characterization of novel (E,E)-1-(4-bromophenyl)-4-(4-methoxyphenyl)buta-1,3-diene, (MeO, Br)-butadiene: a potential dipole-parallel aligned NLO active material

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Abstract

Polar molecules usually crystallize in such a way as to compensate dipole moments. This results from the fact that collinear dipoles prefer parallel alignment while side-by-side dipoles prefer to be antiparallel. This results in the formation of non-polar crystals in most cases. The presence of a large macroscopic dipole moment is one of the criterion necessary for strong non-linear optical (NLO) effects in crystals. By rational design of the molecules, there is a possibility of growing dipole parallel aligned crystals. There are only a few examples where significant dipole parallel alignment has been realized in crystals. Unsymmetrical acetophenone azines (RO-Ph-C(CH₃)=N-N=C(CH₃)-Ph-Y), where R = alkyl, phenyl, and Y = F, Cl, Br, I, are one such class of materials that can result in polar crystals. Complete parallel alignments have been achieved for the methoxy donor (MeO) with Y = Cl, Br, I. But we suspect that the butadiene analogs owing to their larger conjugation length and higher dipole moment would produce stronger NLO effects if perfect dipole parallel alignment can be achieved for them. The 1,3-butadiene analog of the methoxy series of (MeO, Y)-azines is MeO-Ph-CH=CH-CH=CH-Ph-Y and we have successfully synthesized first in the series, (MeO, Br)-butadiene. As expected, the highly conjugated (MeO, Br)-butadiene exhibits fluorescence under UV light as shown in Figure 1. Next step would be the growth of crystals followed by crystal structure solution and refinement via X-ray diffraction. If the butadiene compound is able to crystallize in a polar fashion like azines, it would be a highly active material for NLO, electro-optic and terahertz applications.

Introduction

Polar crystals have long been thought to be difficult or even impossible to produce because side-by-side dipoles tend to prefer antiparallel alignment while colinear dipoles arrange in a parallel orientation in crystals. Thus, the naturally preferred orientation in most crystals is an antiparallel alignment (Figure 1.b). Large-scale polar order is a rare phenomenon and only a few examples of significant parallel dipole alignment have been realized. However, our calculations have shown that parallel dipole aligned lattices may occur as a local minima. Therefore, dipole parallel alignment can be achieved through rational design of molecules.

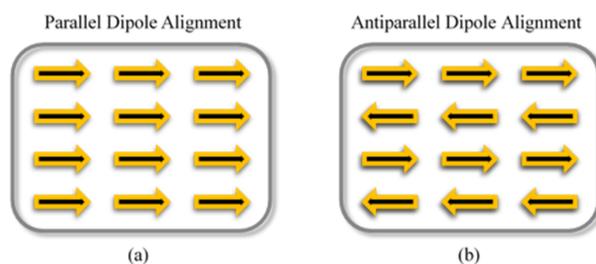


Figure 1

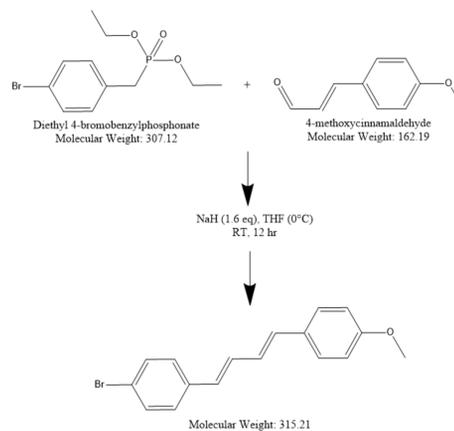
Parallel dipole aligned crystals have been synthesized for a series of unsymmetrical acetophenone azines (RO-Ph-C(CH₃)=N-N=C(CH₃)-Ph-Y), where R = alkyl, phenyl, and Y = F, Cl, Br, I. After this achievement with the azines, it was hypothesized that butadiene analogs could also result in parallel aligned crystals with better non-linear optical properties. Focus was on the 1,3-butadiene analog of the methoxy series of (MeO, Y)-azines (MeO-Ph-CH=CH-CH=CH-Ph-Y). (MeO, Br)-butadiene (Figure 2) was the first to be successfully synthesized, characterized, and crystallized. The crystals of (MeO, Br)-butadiene possessed the parallel dipole alignment assumed in congruence with the azine counterpart.



Figure 2. (MeO, Br)-Azine (left) and (MeO, Br)-Butadiene (right)

Experiment and Results

Synthesis of the butadiene (Scheme 1) was performed in a single-step reaction of diethyl (4-bromobenzyl)phosphonate and 4-methoxycinnamaldehyde in THF with NaH at room temperature.



Scheme 1. Synthesis of (MeO, Br)-butadiene in single-step Wittig Horner reaction.

The (MeO, Br)-butadiene was characterized via ¹H- and ¹³C-NMR. 2D NMR techniques - Heteronuclear Single Quantum Coherence (HSQC) and Correlated Spectroscopy (COSY) were further used to confirm the formation of the product. Figure 3 shows ¹H-NMR of the (MeO, Y)-butadiene measured in deuterated chloroform using a 400MHz liquid NMR instrument.

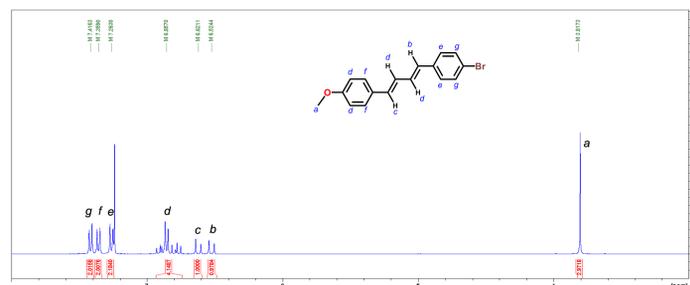


Figure 3. ¹H NMR of (MeO, Br)-butadiene in CDCl₃ solvent (7.260 ppm) at 400MHz.

(MeO, Br)-butadiene displayed blue fluorescence under the short-wave UV light, λ = 254 nm (Figure 4), which was used as a physical characterization method for the solid product to be the desired butadiene.

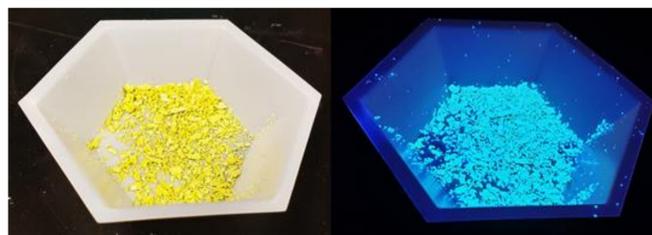


Figure 4. Fluorescence in (MeO, Br)-butadiene when exposed to UV-light (λ = 254 nm).

The pure (MeO, Br)-butadiene product was dissolved in various solvents and set aside for crystallization at room temperature via the slow-evaporation technique. A mixture of 2:1 toluene and chloroform yielded the most reliable crystal formations after several weeks. The butadiene crystals were then analyzed by the X-ray diffraction technique to solve their crystal structure. CSD-Mercury software was used to visualize the 3D crystal structure of the butadiene. The (MeO, Br)-butadiene crystal exhibited near-perfect parallel dipole alignment like that of the azine analog.

Crystal Structure Discussion

Figure 5 shows the near-perfect dipole parallel alignment in (MeO, Br)-butadiene crystals. The crystal structure resembles that of the azine analog, (MeO, Br)-azine. Note that the dipole parallel aligned monolayers which we call PBAMs, Parallel Beloamphiphile Monolayers stack in a zigzag fashion. There is a kink in the crystal structure. This kink is also present in the (MeO, Br)-azine. The reason for the formation of the zigzag pattern results from the presence of directional O---Br bonding interactions at the PBAM surfaces.

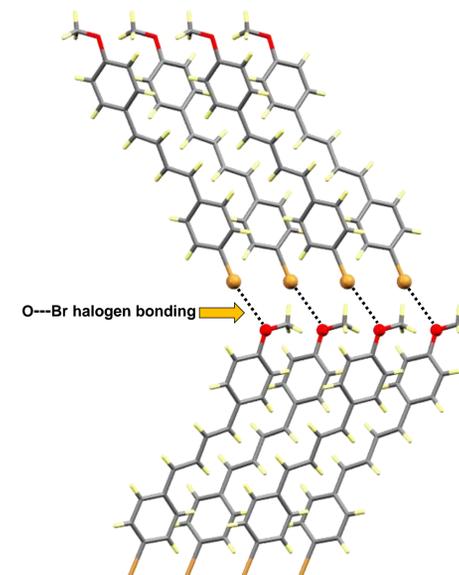


Figure 5. Crystal structure of (MeO, Br)-butadiene. The zigzag pattern emerges due to the directional O---Br halogen bonding between the PBAMs.

Future Work

In ensuing iterations of this process, a number of further experiments and factors will be evaluated to achieve an expanded scope of 1,3-butadienes:

- Expanding the catalogue of butadiene substrates in the series.
 - Synthesis of (MeO, Y)-butadienes to compare with the azines; Y = F, Cl, I, etc.
 - Replacement of MeO group (R) to analyze different series; R = phenyl, biphenyl, nitro, nitrile, etc.
- Study of butadiene compounds and crystals through further analytical instrumental methods; such as fluorescence spectroscopy, mass spectroscopy, FTIR spectroscopy, UV-Vis spectroscopy, etc.
- Observations into increasing the efficiency of the established methodology, in order to provide greater product yields and reliability as well as determine means of study for deviating butadiene substrates.

References

- Perfect Polar Alignment of Parallel Beloamphiphile Monolayers: Synthesis, Characterization, and Crystal Architectures of Unsymmetrical Phenoxy-Substituted Acetophenone Azines, Harmeet Bhoday, Michael Lewis, Steven P. Kelley, and Rainer Glaser, *ChemPlusChem* **2022**, *87*, e202200224.
- (E,E)-1-(4-bromophenyl)-4-(4-methoxyphenyl) buta-1,3-diene, Harmeet Bhoday, Justin Nulsen, Steven P. Kelley, and Rainer Glaser, *CCDC Communication* **2022**, 2203168 (SERFOO).
- Push-Pull Substitution versus Intrinsic or Packing Related N-N Gauche in Azines. Synthesis, Crystal Structures and Packing of Asymmetrical Acetophenone Azines. Grace S. Chen, Jason K. Wilbur, Charles L. Barnes, Rainer Glaser *J. Chem. Soc., Perkin Trans. 2* **1995**, 2311-2317. DOI: 10.1039/P29950002311. ZIFBUL, 1312232, 4-Bromoacetophenone 4-Methoxyacetophenone Azine.