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Topochemical Limits for Solid-State Photoreactivity by Fine Tuning of the $\pi-\pi$ Interactions

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The principal concepts[1] underlying our understanding of the reactivity of bulk solid materials are founded on the topochemical postulate,[2] which essentially employs the necessity of minimum atomic movement in environments with restricted freedom to associate the occurrence of a solid-state reaction and its outcome with structural details in the reacting crystal. Even though this postulate is very intuitive and exceedingly useful, it has been contrasted by very apparent exceptions,[3] a few immediate examples involving the [2 + 2] photodimerization of carbon−carbon double bonds.[4] Similar examples have imposed impediments to the efforts at quantification, and environment-specific effects [e.g., (flexible) reaction cavity, internal pressure and structural rigidity, or hydrogen bonding (HB)] had to be invoked.[5] Even if the generality of the topochemical postulate is its main asset, universality in its compliance is not to be naturally expected, as the plethora of reported results pertain to systems with substantially different chemical and electronic structures, molecular geometries, and properties; utilization of only one molecule, preferably in an identical electronic form, in different, well-defined structural environments to probe the structural aspects of photoreactivity appears to be a much more viable approach.[6] However, reported examples of molecules existing as more than two photoreactive polymorphs or solvates are extremely rare. With as many as six new "pseudopolymorphic" crystalline forms of a simple organic acid, five of which are photoreactive, we report herein the utility of intermolecular interactions for controlling the photodimerization by fine-tuning of the $\pi-\pi$ interactions at the limits of the geometric criteria for solid-state reactivity. This first report on the solid-state photochemistry of the bisstyrylbenzene moiety[7] demonstrates, in a much more direct way than has previously been assumed, the effect of subtle structural factors on the reactivity toward photodimerization of double bonds in the crystalline state.

For this purpose, we employed bisstyrylbenzene dicarboxylic acid [1,3-phenylene-3,3′-bis(2-propenoic) acid], H_2BSBDA (Figure 1), which was envisaged to be a molecule suitable for supramolecular self-templating into a photoreactive orientation.[8] As it is constrained to all-molecule planarity by the extended π conjugation, H_2BSBDA is a rigid π system of extremely limited packing freedom: C_{2v}-symmetry-imposed head-to-head stacking of infinite $R_2^2(8)$ HB tapes is the only foreseeable pattern in a solventless crystal. The potential for supramolecular interactions is restricted to strong HB of the carboxylic termini and weak $\pi-\pi$ stacking interactions of the bisstyrylbenzene portion; any modification of the former will be reflected in minute alterations of the latter interactions. Because when all of the other parameters have nearly identical values the reactivity is expected to be determined by the distance between the olefinic bonds, such HB-directed tuning of the $\pi-\pi$ stacking is expected to alter the reaction outcome.

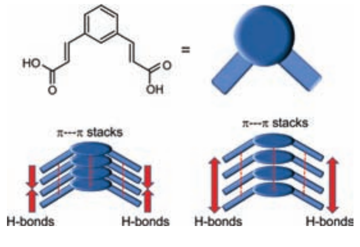
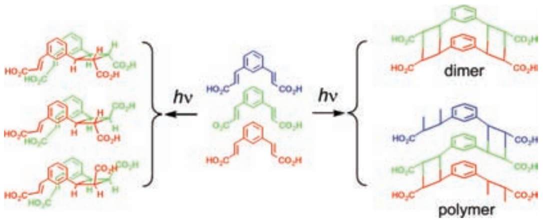


Figure 1. Structure of H_2BSBDA and schematic illustration of the proposed control over the secondary interactions ($\pi-\pi$) by modulation of the primary interactions (hydrogen bonds of the carboxylic groups).

Besides serving as a "photochemical probe" for reactivity, H_2BSBDA may also provide solventless access to a myriad of useful carboxy-functionalized synthetic intermediates by having two photoreactive groups (Scheme 1): one-center reaction would result in phenyl-substituted β-truxinic acids, and two-center *bi*molecular reaction would provide access to very rare [2,2]metacyclophanes, whereas *multi*molecular reaction would afford alternating *m*-phenylene−cyclobutane copolymers.

Scheme 1. Possible One-Center (left) and Two-Center (right) Reaction Pathways for Head-to-Head-Stacked Molecules of H_2BSBDA



Exhaustive screening with IR monitoring for polymorphs and solvates of H_2BSBDA afforded six solid forms (A−F), five of which (A−E) were crystallographically authenticated: A and B are unsolvated polymorphs, D and E are 1:1 and 2:1 dioxane solvates, and C is a monohydrate that exists as the hydroxonium hydrogen salt $(H_3O)^+(HBSBDA)^-$ (Figure 2 and Table S1 in the Supporting Information). Structures A−D share the expected head-to-head, parallel-displaced stacking, with one of the two shorter cell axes coincident with the stacking direction and HB chains stretching close to the direction of the longest axis. The simplest repeating motif among the forms A−D, a HB dimer around an $R_2^2(8)$ synthon translated into a zigzag tape (and hence the shortest long axis) is observed in form B (Figure 3). In contrast, in form A, only one of the two carboxylic groups is $R_2^2(8)$-bonded, whereas the other one bridges two molecules of a catemer in a $C(4)$ arrangement. The head-to-head aromatic stacking is also present in form C, but the alternating $HBSBDA^-$ ions are bridged over an equidistant proton and inclined to each other (60°). Each oxonium ion assists the stacking by crisscrossing two pairs of carboxylic groups from

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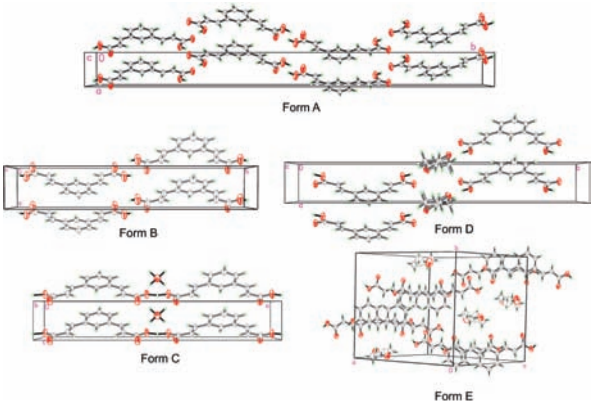

Figure 2. ORTEP-style crystal packing diagrams, at 50% probability, of the five crystallographically authenticated forms of H_2BSBDA.

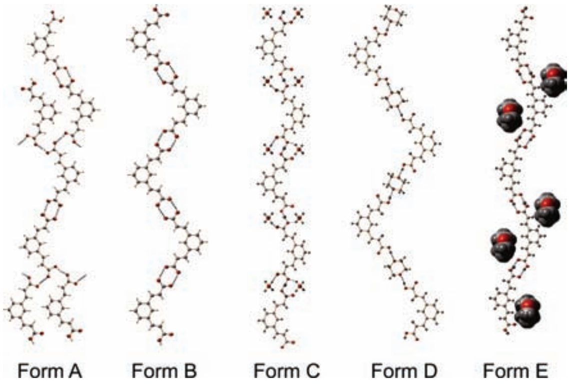

Figure 3. HB motifs in the crystals of the five forms of H_2BSBDA (the disordered dioxane molecules in form E are shown as space-filling models).

neighboring chains. As in A and B, the zigzag tapes in form D are planar, but the $R_2^2(8)$-bonded H_2BSBDA molecules are spaced by $R_2^2(7)$-bridging dioxane molecules. As a result, the acid molecules are separated beyond the usual $\pi-\pi$ stacking distance. Although the planar zigzag tapes also appear in form E, the dioxane molecules cause slippage of the tapes, so the aromatic rings from adjacent tapes are isolated ($d > 4.1$ Å).

The IR spectra clearly showed that, except for form E, all forms of H_2BSBDA exposed to UV light are photoreactive (Figure S1 in the Supporting Information). The evolution of multiple peaks at 3.6−4.2 and 6.1−7.1 ppm in the ^1H NMR spectra (Figure S2) confirmed the creation of cyclobutane products. On the basis of the NMR results, it was concluded that short-term irradiation (1 h) of forms A, D, and F results in identical products that differ from those obtained from each of forms B and C. HPLC and NMR analyses showed that the products obtained after long exposures (6 h), which appear from methanol as thick glassy matrices of good solubility in basic aqueous solutions, are of mixed composition. In addition to the dimer $(H_2BSBDA)_2$ as the main product, oligomeric species up to the hexamer $(H_2BSBDA)_6$ were detected by electrospray ionization mass spectrometry (ESI-MS) (Figure S3).

The activity of forms A−D corresponds to the general geometric criteria for photodimerization (Chart 1), but instead of the commonly accepted approximate bond-center-to-bond-center distance criterion for reactivity ($d \approx 4$ Å), for the special case of parallel double bonds it sets *the lower limit of nonreactive bonds* to the more precise value $d = 4.0165$ Å. This means that all parallel double bonds separated by less than 4.0165 Å are reactive. In view of the possibly different reaction pathways (Scheme 1) and differences in the two angles related to the relative orientation of reactive bonds (θ_2 and θ_3), the estimated yields (^1H NMR) faithfully reflect the center-to-center distances d (Table 1): tuning the $\pi-\pi$ stacking from 3.876(2) Å to 4.0165(2) Å decreased the yield from 45−57% to 20% after 1 h and from 83−100% to 50% after 6 h of irradiation. A representative case is provided by forms A and D, with parallel olefinic bonds that differ in their separation by only 0.123(3) Å: while the closer olefinic bonds (A) reacted almost completely after 6 h, only half of the more distant bonds (D) dimerized in that time. As demonstrated with form E, a bond separation of 4.144(1) Å rendered the system completely photoinert, but the effect in this case may have been augmented by the interbond skewing ($\theta_1 = 49.0°$). However, on the basis of the nearly identical increments in d in going from A to D [0.123(3) Å] and from D to E [0.128(3) Å], the former of which reduced the reactivity by a notable 25%, it appears that the increased bond separation d alone is sufficient to account for the inertness of form E.

Chart 1. Definitions of the Parameters Usually Considered To Be Geometric Criteria for [2 + 2] Photodimerization of Double Bonds (According to Ref 11; θ_3 is the Angle between the >C=C< and C=C−C=C Planes)

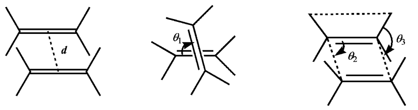

Table 1. Geometric Parameters of H_2BSBDA Polymorphs and Solvates Relevant to the Mechanistic Aspects of Photodimerization (Parameter Definitions Are Given in Chart 1)

form	d (Å)^a	θ_1 (deg)^a	θ_2 (deg)^a	θ_3 (deg)^a	yield (%)^b	$n^{b,c}$
A	3.8933(1)	0	102.4(2)	59.7(2)	45; 99	>1
B	3.876(2)	0	117.7(2)	87.4(2)	57; 100	>1
C	3.8806(2)	0	116.2(3)	86.6(3)	57; 83	1
D	4.0165(2)	0	114.2(2)	89.6(2)	20; 50	>1
E	4.144(1)	49.0(1)	111.0(1)	92.3(1)	0	0
F^d	–	–	–	–	20; 25	1
Ideal	<4.0	0	90	90	100	1

^{a} The errors are based on the lattice parameters. ^{b} Based on unreacted H_2BSBDA after 1 and 6 h (^1H NMR). ^{c} Number of products after 1 h. ^{d} The structure was not determined.

Another important conclusion from this work is that for practically equal distances [3.8806(2) and 3.876(2) Å] at long irradiation times (6 h), the anion $HBSBDA^-$ in C is less reactive than the neutral form H_2BSBDA in B (83 vs 100%), although at short irradiation times (1 h) they react to the same extent (57%). Thus, the reaction profile is also affected by the charge on the reactant; the reaction of the anion is slower but more selective, affording smaller yield of a single product.

Direct evidence for the dimerization was provided by single-crystal X-ray photodiffraction analysis[9] of ex situ UV-irradiated single crystals. The ring substituents in single crystals of forms A and B, reacted by exposure to UV radiation to 17% (0.50 h) and 36% (0.33 h), respectively, showed triple disorder corresponding to the formation of cyclobutane rings in the products above and below the molecular plane (Figure 4). The reacted crystals of form B contain a fourth component related to flipping of the substituents around the double bond. At this early stage, when the reaction is still confined within ordered lattice, A and B yield different products: while both mirror-related double bonds of H_2BSBDA in form B react, only one bond in form A is dimerized. Thus, the longer stacking distance in A than in B not only affects the reaction yields but also directs the qualitative outcome of the reaction. The reasons behind the difference in reactivity can be traced back to the HB: similar to both olefinic bonds in B, only the bond adjacent to the dimeric carboxylic group in form A is reactive, while the bond adjacent to the carboxylic group involved in

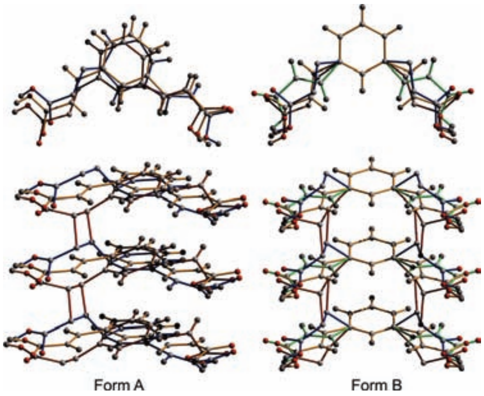

Figure 4. Ball-and-stick plots of UV-reacted structures (~17% and 36%) of forms A and B. The cyclobutane hydrogen atoms have been omitted, and the three main components in each structure are colored brown, blue, and ochre for clarity (the flipped arms in the structure of form B are colored green). The complex disorder of the benzene ring in B was not treated in the refinements.

the catemer HB motif is inert. Comparison of the $\pi-\pi$ distances in the products (3.784−3.875 Å in A, 3.827 Å in B) with the values observed in cyclobutane-bridged metacyclophanes ("*m-m* cyclb' in Figure S4) shows that the products are dimers and oligomers rather than cyclophanes. As illustrated by the structure of A after one-center reaction (Figure 4), the second cyclization is prevented by benzene-ring tilting that is caused by the closure of the butane ring and increases the separation between the unreacted olefinic bonds.

The mechanism of the reaction can be understood in terms of the Woodward−Hoffmann (WH) rules,[10] which state that a pericyclic reaction is allowed if the occupied orbitals in the reactants and in the product are of identical symmetry. According to these rules, the suprafacial cycloaddition of the double bonds of ethylene, to which each of the π-stacked α,β-olefinic bonds in H_2BSBDA can be reduced, is thermally forbidden because of the unfavorable alignment of the regions with identical signs for the second-order Fukui function. However, for photochemical reactions such as the one studied here, the WH rules are inverted, and the suprafacial cycloaddition becomes possible.

In conclusion, by utilizing a pseudopolymorphic series of six solid forms of a single planar dicarboxylic acid as a low-dimensional supramolecular entity able to self-template, in this first study of the solid-state photochemistry of the bisstyrylbenzene moiety we have assessed the effect of several structural factors on photodimerization reactivity. We have shown that the distance between the reactive olefinic bonds (d) has a comparably greater effect on the yield and distribution of the products than either slippage (θ_2) or inclination (θ_3) of the bond planes relative to each other. Although the agreement is only semiquantitative, the decreasing trend of the photochemical yield corresponds well with the increasing bond separation. From the present set of structures, it is concluded that all *parallel* double bonds separated by $\leq$4.0165 Å are reactive. Bonds with d slightly larger than this value may be (but are not necessarily) reactive. The inactivity is facilitated by relative twisting of the bonds ($\theta_1 \neq 0$). On the basis of the semiquantitative correlations for the photoreactive forms and the similarity of the yields of forms F and E, the distance between the olefinic bonds in form F, whose structure could not be determined, is predicted to be $\geq$4.01 Å. The reactivity is also affected by the charge (neutral or ionic) of the reacting molecule and specific intermolecular interactions in which the reactive functionality participates. At equal bond separation, the reaction between parallel olefinic bonds in an anion is slower but more selective than that in the respective neutral molecule. As evidenced by X-ray photodiffraction analysis of forms A and B, only the olefinic bonds adjacent to carboxylic groups involved in dimeric HB react, while those associated with polymeric HB (form A) are inert. The difference in energy required for breaking of the HB and alternative deexcitation pathways can be suggested as possible reasons. The product analysis showed that the photoreaction affords bis(*m*-phenylene)cyclobutane dimers as main products, accompanied by *m*-phenylene−cyclobutane oligomers with up to six units, without detectable cyclophane structures. This result shows that unlike the solution-state reaction,[7] in the solid state the bisstyrylbenzene unit prefers one-center reaction over simultaneous reaction at both centers. This is prescribed to an unfavorably distorted disposition of the unreacted olefinic bonds between the singly reacted molecules. This and similar systems are of synthetic importance, as they can provide facile, solventless access to rare, functionalized alternating *m*-phenylene−cyclobutane oligomer topologies.

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Supporting Information Available: Experimental details, crystallographic data (tabular and CIF), and IR, NMR, and ESI-MS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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