spectrum of the Cl_2^- anion produced by charge transfer interaction between alkali metal atoms and chlorine molecules. The Cl_2^- fundamentals observed here in solid argon range between 225 and 264 cm^{-1} depending upon the alkali cation; these values are in good agreement with the 265-cm^{-1} Raman assignment[3] to Cl_2^- in glassy matrices. The small alkali metal effect indicates the presence of the alkali metal in the scattering species; the most probable reaction product is $M^+Cl_2^-$.

Holzer, *et al.*,[9] have discussed the experimental characteristics of resonance excitation spectra for halogen gases. Clearly, the present resonance emission spectra could be due to resonance fluorescence or resonance Raman. If the high measured depolarization ratios are due to molecular orientation effects, the most prominent identifying characteristic of these spectra is the series of lines with regularly decreasing intensities with increasing vibrational quantum number as is shown in Figure 1. This criterion[9] suggests that the present emission spectra are probably due to the resonance Raman effect.

The equation $E(v) - E(0) = \omega_e v - \omega_e X_e(v^2 + v)$ given by Herzberg[12] is commonly used to calculate energy levels for diatomic anharmonic oscillators. The frequency data of Table I were fit to this equation using a least-squares analysis which produced the average vibrational constants $\omega_e = 249.2 \pm 1.0$ and $\omega_e X_e = 1.62 \pm 0.1$ cm^{-1} for $^{35}Cl_2^-$. The calculated and observed fundamentals and overtones are compared in Table I. Note that the average discrepancy between calculated and observed frequencies is less than 1 cm^{-1}.

The Cl_2^- fundamental frequency observed here is near 250 cm^{-1} depending on the alkali cation; the Cl_2 precursor fundamental was 539 cm^{-1}, approximately double the Cl_2^- fundamental. An analogous relationship has been reported for F_2 (892 cm^{-1}) and F_2^- (460 cm^{-1}).[1] The anion electron in these species is, of course, antibonding, which reduces the net bond order from 1 to $^1/_2$ when X_2 is reduced to X_2^-. It is not surprising that the X_2^- frequency is approximately half of the X_2 fundamental.

Acknowledgment. The authors gratefully acknowledge financial support for this research under Grant GP-28582 and instrument support under Grant GP-18251 of the National Science Foundation and helpful discussions with Dr. H. J. Bernstein.

(12) G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed, Van Nostrand, Princeton, N. J., 1950, p 93.

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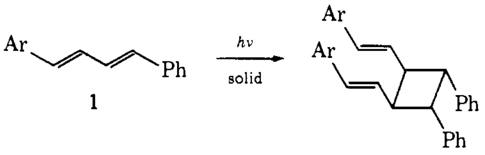
Reactions in Chiral Crystals. Optically Active Heterophotodimer Formation from Chiral Single Crystals

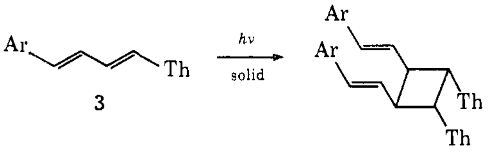
Sir:

We report a novel, absolute asymmetric synthesis in which a lattice-controlled photocycloaddition reaction within a two-component single crystal affords a chiral mixed dimer. This constitutes the second example of a successful optical synthesis where the sole chiral element is the enantiomorphic space group of the crystal in which the reaction takes place.[1,2]

1-(2,6-Dichlorophenyl)-4-phenyl-*trans,trans*-1,3-butadiene (**1**) crystallizes as colorless needles, mp 107°, with crystallographic constants $a = 9.39$, $b = 4.00$, and $c = 35.30$ Å, space group $P2_12_12_1$, and four molecules per unit cell. Irradiation of **1** in the solid state through Pyrex yields a single photoproduct, the mirror-symmetric dimer **2**.[3] The thiophene analog of **1**, 1-(2,6-dichlorophenyl)-4-thienyl-*trans,trans*-1,3-butadiene (**3**), crystallizes as yellow needles, mp 81°, and is isomorphous with **1**, having crystallographic constants $a = 9.15$, $b = 3.99$, and $c = 34.98$ Å, space group $P2_12_12_1$, and four molecules per unit cell. On irradiation under the above conditions **3** also affords the topochemically expected photodimer **4**.



1 **2**



3 **4**

Th = 2-thienyl and Ar = 2,6-$C_6H_3Cl_2$

Compunds **1** and **3** form mixed crystals (substitutional solid solutions) upon cooling from the melt or on crystallization of an ethanolic solution of the two.[4] Irradiation of a *polycrystalline* sample of mixed crystals of **1** and **3** yields the *racemic* mixed dimer **5**, mp 93–94°.[5] The formation of dimers **2** and **4** can be minimized in this experiment by using a small (*ca.* 15%) amount of the thiophene compound **3**, which absorbs at slightly longer wavelengths than does the phenyl compound **1**,[6] and irradiating through appropriate cut-off filters so that, ideally, only **3** absorbs light; the dilution of **3** minimizes the number of **3**···**3** contacts in the crystal (which lead to **4**) while lack of excitation of **1** prevents formation of **2**.[7]

(1) K. Penzien and G. M. J. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **8**, 608 (1969).

(2) The suggestion that the formation of unequal amounts of enantiomers might result from the irradiation of a two-component chiral single crystal, in a system such as that described herein, was first made by Dr. M. Lahav of this department. The chemical and crystallographic requirements for asymmetric synthesis *via* topochemically controlled solid-state photodimerization in one-or two-component chiral single crystals have been comprehensively analyzed: B. S. Green, M. Lahav, and G. M. J. Schmidt, to be submitted for publication.

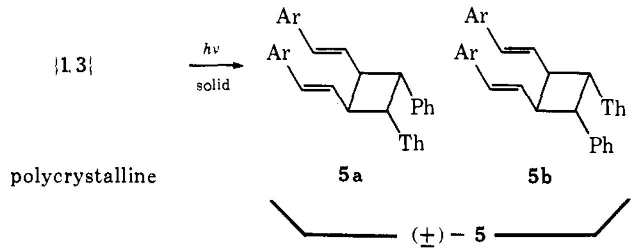
(3) M. D. Cohen, A. Elgavi, B. S. Green, Z. Ludmer, and G. M. J. Schmidt, *J. Amer. Chem. Soc.*, **94**, 6776 (1972).

(4) Debye–Scherrer powder photographs of such mixed crystals indicate the same crystal structure as that of the constituents.

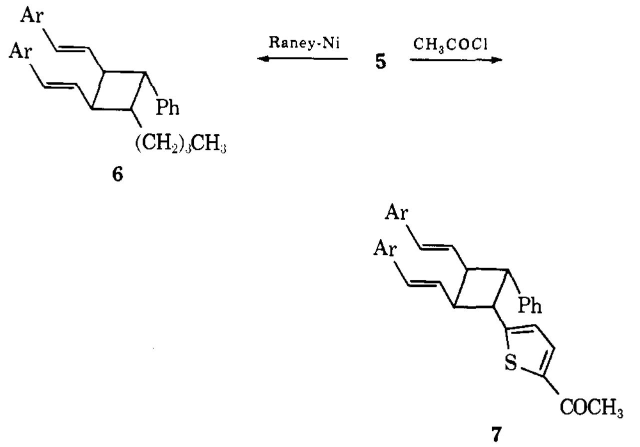
(5) Nmr: $\delta_{TMS}^{CDCl_3}$ 3.7–4.2 (4 H, m, cyclobutane), 6.5 (4 H, m, =CH—), 7.0 (14 H, m, aromatic); ir: 960 cm^{-1} (*trans*-CH=CH); mass spectrum, *m/e* 554 (M^+, Cl_4), 368 [$C_6H_3Cl_2(CH{=}CH)_3C_6H_3Cl_2$, 11%], 280 [$C_6H_3Cl_2(CH{=}CH)_2C_4H_3S$, 100%], 274 [$C_6H_3Cl_2(CH{=}CH)_2$-$C_6H_5$, 85%], 186 [$C_6H_5CH{=}CHC_4H_3S$, 39%].

(6) **1**, λ_{max}^{EtOH} 317 nm ($\epsilon \sim 3.6 \times 10^4$); **3**, λ_{max}^{EtOH} 335 nm ($\epsilon \sim 3.4 \times 10^4$).

(7) (a) This would not be the case were there efficient energy transfer from photoexcited **3** to **1**. This energetically "uphill" process was not expected to be predominant, and our results indicate that it is indeed inefficient. (b) In practice, irradiation conditions usually allow some uv absorption by the tail of **1** so that typical results are: crystals containing 0.85 g of **1** and 0.15 g of **3** yield 0.25 g of dimeric material (**2**, **4**, and **5**) which is comprised of *ca.* 90% **5**.



We wished to establish whether photoexcited molecules of **3** contained in stacks of **1** would exhibit differences in reactivity of their "upper" and "lower" faces during reaction (Figure 1) to give **5a** and **5b**, respectively. (The crystal structure of **1** has been determined in this laboratory[3,8] and Figure 1 was constructed by simply substituting a thiophene for a phenyl within the stacks of **1**. The ground-state perturbation to translational symmetry produced by inclusion of guest molecules of **3** is, we believe, small and the ratio of **5a** to **5b**, *i.e.*, the optical yield of the reaction, will primarily reflect the nature of the excited state of **3** responsible for cyclodimerization.) For this purpose we prepared, by growth from the melt in evacuated glass bulbs,[9] large (1–6 g) *single* mixed crystals containing 15% of **3** in **1**, which were powdered and irradiated as above. The resulting mixed dimer **5** was consistently found to possess optical activity, some crystals affording dextrorotatory and some levorotatory material, [α]D + or − *ca.* 1°.[10] Transformation of optically active **5** to a less symmetrical molecule led to many-fold enhancement of specific rotation. Raney nickel reductive degradation of the thiophene group in (+)-**5** [or(−)-**5**] led to (−)-**6** [or (+)-**6**], [α]D *ca.* 10°,[11] while acetylation of (+)-**5** afforded (+)-**7**,[12] [α]D *ca.* 5°.



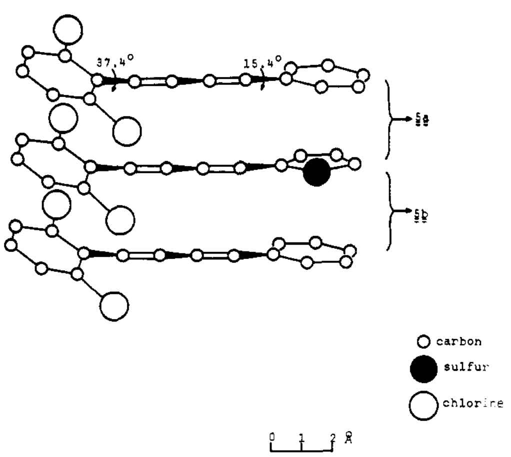


Figure 1. Packing diagram of a mixed crystal of **1** and **3**, based on the crystal structure of **1**[3,8] showing the intermolecular contacts which lead to the enantiomeric photodimers **5a** and **5b**.

Currently, the optical yield of this reaction is being established and the absolute configuration of a given single mixed crystal (*i.e.*, whether the stacks of molecules are twisted as in Figure 1 or as in its mirror image) and of the dominant cyclobutane photoproduct (*i.e.*, **5a** or **5b**) from that crystal, or one having the same handedness, are being determined. When complete, this information will indicate which face of a diaryl butadiene of structure **1** or **3** is the more reactive one in this system and will provide insight into the reaction coordinate as ground-state molecules, initially separated by 4 Å, move to a final bonding distance of 1.5 Å.

Finally, the simple production of stable, optically active samples from optically inactive starting material is highly relevant to current hypotheses on the prebiological origin of optical activity on earth.[13]

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(8) We thank Dr. D. Rabinovich and Z. Shaked for providing us with the crystal structure data for **1**. A table of atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-2058. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(9) J. N. Sherwood, and S. J. Thomson, *J. Sci. Instrum.*, 37, 242 (1960). We are most grateful to Dr. Joel Bernstein, Professor M. D. Cohen, and Z. Ludmer for help in constructing this apparatus and for much useful advice.

(10) Measured on a Perkin-Elmer Model 141 polarimeter in chloroform with 1-ml, 1-dm cuvettes. Values for α_{obsd} (mg of **5**): 0.076° (67), 0.070° (66), −0.076° (100).

(11) Colorless oil, *m/e* 528 (M^+, Cl_4), 368 [$C_6H_3Cl_2(CH{=}CH)_3C_6H_3Cl_2$, 3%], 274 [$C_6H_5(CH{=}CH)_2C_6H_3Cl_2$, 80%], 254 [$C_6H_3Cl_2(CH{=}CH)_2C_4H_9$, 100%], 160 [$C_6H_5CH{=}CHC_4H_9$, 48%].

(12) Almost colorless solid, mp 121–122°; nmr: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 2.4 (3 H, s, CH_3), 3.8–4.3 (4 H, m, cyclobutane CH), 6.5 (4 H, m, =CH—), 7.2 (13 H, m, aromatic).

(13) We note that the use of single crystals is not essential for the success of these experiments. Irradiation of polycrystalline samples prepared by slow evaporation of an ethanolic solution of **1** and **3** also affords optically active **5**, albeit of lower specific rotation. This is apparently due to self-innoculation by a relatively small number of initial nuclei. Rapid formation of mixed crystals of **1** and **3** generally led to racemic **5**.

(14) Ph.D. student of the Feinberg Graduate School.

(15) Deceased July 12, 1971.

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General Base Catalyzed Intramolecular Transesterification

Sir:

The α-chymotrypsin-catalyzed hydrolysis of esters and amides involves acylation of serine-195, with release of the alcohol or amine portion of the substrate, followed by deacylation to regenerate active enzyme.[1] The generally accepted mechanism for the

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(1) T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," Vol. I, W. A. Benjamin, New York, N. Y., 1966, Chapter 2; M. L. Bender, "Mechanisms of Homogeneous Catalysis from Protons to Proteins," Wiley, New York, N. Y., 1971.