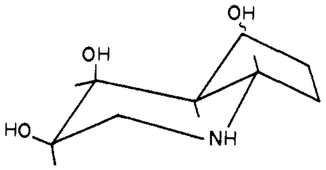
with both ninhydrin and nitroprusside.[7] Significant retardation of **2** on borate-impregnated thin-layer systems and reaction of the compound with periodate were suggestive of a *vic*-glycol moiety in the molecule.[8]

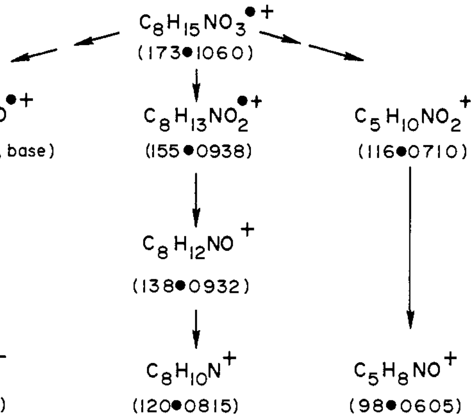
Structure **2** was assigned on the basis of nmr spin decoupling.[9] The single proton H-4a (δ 2.05, m) is coupled to H-4 (δ 4.60, d of d, J = 3 Hz), to H-5 (δ 4.19, m, J = 6.5 Hz), and to H-7a (δ 3.05, m, J = 9 Hz). The secondary carbinol proton H-5 is coupled to a high-field proton (δ 2.27, m). H-7a is also coupled to one or more high-field protons at δ 1.71 (m). H-3 (δ 4.50, apparent d of d) is coupled to H-2_{ax} (δ 2.57, d of d, J = 7 Hz) and to H-2_{eq} (δ 3.23, d of d, J = 2 Hz); H-2_{ax} and H-2_{eq} are in turn coupled to each other (J = 12 Hz).

The fusion of the two rings is trans; H-4a and H-7a are both axial ($J_{4a,7a}$ = 9 Hz).[10] Since $J_{4,4a}$ = 3 Hz and H-4a is axial, H-4 is necessarily equatorial. Since H-3 is axial ($J_{2ax,3}$ = 7 Hz), the *vic*-glycol is cis ($J_{3,4}$ = 4.5 Hz). The configuration at C-5 could not be assigned with certainty from the coupling constants observed. From the available data, the configuration of **2** is either **3** (3*R*, 4*S*, 4a*R*, 7a*S*) or its enantiomer. The major fragments observed in the high-resolution mass spectrum of **2** (see Scheme I) are in accord with the assigned structure.



3

Scheme I



Acetylation[11] of **2** gave rise to the 1,3,5-triacetyl derivative in quantitative yield [*m/e* 299 (M), 239 (M − HOAc), 179 (M − 2HOAc), 137 (M − 2HOAc − C_2H_2O), 120; nmr δ 2.09 (9 H, s), 5.04 (H-4, d of d, $J_{3,4}$ = 4.5 Hz), 5.39 (H-5, m), and 5.70 (H-3, apparent d of d); ir 3420 (OH), 1740 (ester), and 1630 cm^{-1} (amide); no reaction with ninhydrin; one proton exchanged with D_2O (mass spectrometry)]. The remaining hydroxyl group (C-4) resisted acetylation (probably as a result of steric hindrance imposed upon this position by the adjacent acetoxy groups) and CrO_3–pyridine oxidation.[12]

Table I. Per Cent Incorporation of Precursors into **2**

Compd (sp act., μCi/μmol)	μmol added/ culture[a]	Incorpn, %[b]
DL-[6-^{14}C]Aminoadipic acid (11.7)	0.4	1.8
DL-[1-^{14}C]Lysine (2.7)	2.9	5.2
DL-[2-^{14}C]Lysine (0.02)	711.0	11.0
DL-[6-^{14}C]Lysine (2)	2.3	15.1
L-[U-^{14}C]Lysine (1.9)	3.2	5.9
DL-[4,5-^{3}H]Pipecolic acid (0.6)	45.8	3.2
DL-[*ring*-^{3}H]Pipecolic acid (250)	0.8	8.8
DL-[1-^{14}C]Pipecolic acid (0.006)	386.0	4.2

[a] Cultures, grown in 1-l. Roux flasks as previously described,[2] were drained at 12 days of age and resuspended in 50 ml of water containing the appropriate test compound. After 48 hr, mycelia were recovered and extracted with ethanol. [b] The product **2** was isolated by ion-exchange chromatography[6] and counted; % incorporation = (dpm of **2** recovered/dpm of compd added) × 100.

Preliminary experiments (Table I) indicate that the biosynthesis of **2** parallels that of slaframine.[2] The carbon skeleton of pipecolic acid appears to be incorporated *in toto;* the pathway 2-aminoadipic acid → L-lysine → pipecolic acid → **2** is probably operative. The origin of the remaining two carbons, C-5 and C-6, is unknown (DL-[1-^{14}C]- and DL-[3-^{14}C]serine, possible sources, were not incorporated). This biosynthetic route is at variance with those of other piperidine ring systems arising from poly-β-keto acids (coniine, conhydrine),[13] from dihydroxyphenylalanine (betanin),[14] and from isoprenoid precursors (as in the 2-pyrindine alkaloid skytanthine).[15]

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[7] D. Waldi in "Thin Layer Chromatography," E. Stahl, Ed., Academic Press, New York, N. Y., 1965, p 497.

[8] J. Böeseken, *Advan. Carbohyd. Chem.*, **4**, 189 (1949).

[9] Varian XL-100, D_2O (D_2O lock). All shifts reported in parts per million relative to TMS.

[10] R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Amer. Chem. Soc.*, **80**, 6098 (1958).

[11] R. C. Pandey, V. F. German, Y. Nishikawa, and K. L. Rinehart, Jr., *ibid.*, **93**, 3738 (1971).

[12] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarrett, *ibid.*, **75**, 422 (1953).

[13] (a) E. Leete, *Accounts Chem. Res.*, **4**, 100 (1971); (b) "Biogenesis of Natural Compounds," P. Bernfeld, Ed., Pergamon Press, Oxford, 1967, p 961; (c) *J. Amer. Chem. Soc.*, **85**, 3523 (1963); (d) *ibid.*, **86**, 2509 (1964).

[14] H. E. Miller, H. Rösler, A. Wohlpart, H. Wyler, M. E. Wilcox, H. Frohofer, T. J. Mabry, and A. S. Dreiding, *Helv. Chim. Acta*, **51**, 1470 (1968).

[15] (a) H. Auda, H. R. Juneja, E. J. Eisenbraun, G. R. Waller, W. R. Kays, and H. H. Appel, *J. Amer. Chem. Soc.*, **89**, 2476 (1967); (b) H. Auda, G. R. Waller, and E. J. Eisenbraun, *J. Biol. Chem.*, **242**, 4157 (1967).

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Resonance Raman Spectrum of the Matrix-Isolated Chlorine Molecular Anion Cl_2^-

Sir:

Argon matrices at 15–20°K have proven a fruitful means of trapping reactive intermediates, and recent[1]

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[1] W. F. Howard, Jr., and L. Andrews, paper submitted for publication.

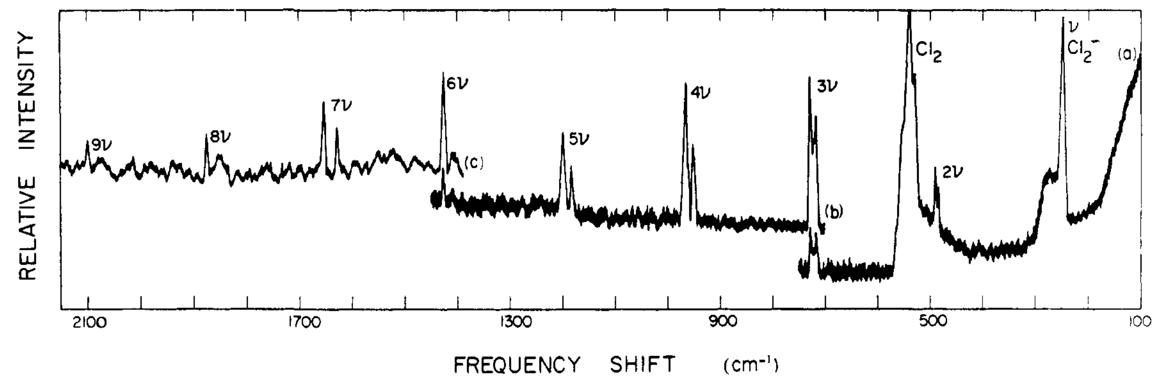

Figure 1. Resonance Raman spectrum of the products of chlorine molecule–lithium atom matrix reactions. Ar/Cl_2 = 100. Instrumental parameters: exciting line approximately 50 mW of 5145 Å; range (a) 1 × 10^{-9} A, (b) 0.3 × 10^{-9} A, (c) 0.1 × 10^{-9} A; filter, 5 Å dielectric spike; rise time (a) 1 sec, (b) 3 sec, (c) 10 sec; scan speed, 10 cm^{-1}/min.

success with fluorine–alkali metal reactions producing $M^+F_2^-$ has suggested a search for the chlorine anion Cl_2^- in a similar fashion. The existence of Cl_2^- has been noted in the electron spin resonance spectrum of γ-irradiated KCl.[2] Hass and Griscom[3] have attributed a Raman band at 265 cm^{-1} in γ-irradiated alkali halide–alkali borate glasses to the Cl_2^- fundamental. Person[4] has estimated properties of the chlorine molecular anion, and Minturn, *et al.*,[5] have proposed an $M^+Cl_2^-$ intermediate in crossed molecular beam reactions.

The experimental technique, with spectroscopic and cryogenic equipment, has been described previously.[6,7] An argon–chlorine sample (Ar/Cl_2 = 100) was deposited on a tilted copper wedge maintained near 15°K at a rate of 2 mmol/hr. Simultaneously, an atomic beam of alkali metal was directed at the wedge, using metal vapor pressures near 1 μ. Raman spectra from 50 to 2250 cm^{-1} were recorded on a Spex Ramalog using the 4880- and 5145-Å excitation lines from a Coherent Radiation argon plasma laser with about 50 mW of power at the sample.

The argon matrix Raman spectrum of Cl_2 (Ar/Cl_2 = 100) was recorded. The only observed spectral feature was the molecular chlorine band partially resolved into isotopic components at 538.6, 531.0, and 523.2 ± 1.0 cm^{-1} for the 35–35, 35–37, and 37–37 isotopic pairs, in agreement with the solid[8] $^{35}Cl_2$ fundamental of 540 cm^{-1} and a shift of 16 cm^{-1} from the 554-cm^{-1} gas-phase value[9] for $^{35}Cl_2$. Depolarization ratio measurements for argon matrix-isolated Cl_2 were 0.62 and 0.64; these values are somewhat higher than the gas-phase[9] value of 0.14 presumably due to the scrambling effect of the frosty matrix on the Raman scattered signal and to preferential molecular orientation in the matrix sample.

No discrete bands were observed when lithium or sodium–argon samples were studied with laser excitation. These samples, which were dark gray or black, produced only a continuous background.

Matrix reactions of alkali metal atoms with Cl_2 molecules were studied extensively: these samples were orange colored. Since the absorption spectrum for compounds of this color includes the blue-green region, the resonance excitation of these samples with the 4880- and 5145-Å argon ion laser lines is not surprising. Na–Cl_2 argon matrix samples produced a prominent signal shifted 225 ± 1 cm^{-1} below the 4880- and 5145-Å exciting lines; the first overtone appeared at 448 ± 1 cm^{-1}. The intense 225-cm^{-1} signal was depolarized (ρ measurements 0.88, 0.92). These signals showed a dependence upon the alkali metal reagent. the intense fundamental was observed at 246 cm^{-1} with Li, 264 with K, 260 with Rb, and 259 ± 1 with Cs. The cesium–chlorine reaction product produced a series of overtones at 516, 767, and 1018 cm^{-1}. These emission lines were depolarized; ρ measurements ranged from 0.78 to 0.86. In several spectra, a shoulder appeared at 273 ± 2 cm^{-1} which is tentatively assigned to the Cl_3^- symmetric stretching mode, in agreement with the ν_1 assignment of Evans and Lo.[10] Regions corresponding to the argon matrix frequencies[11] of LiCl and NaCl were void of signal, as expected for highly ionic molecules.

The argon matrix reaction of Li and Cl_2 produced a distinct orange-red color and the longest series of overtones observed in this work. Figure 1 shows the 246-cm^{-1} fundamental and eight overtones with five of the overtones showing isotopic splittings; Table I lists the observed fundamental frequency and overtones.

We assign the observed bands to the resonance Raman

Table I. Observed and Calculated Vibrational Frequencies in the Resonance Raman Spectrum of Cl_2^- in the $Li^+Cl_2^-$ Species

	$(^{35}Cl_2)^-$		$(^{35}Cl^{37}Cl)^-$	
	ν_{obsd}, cm^{-1}	ν_{calcd}, cm^{-1}	ν_{obsd}, cm^{-1}	ν_{calcd}, cm^{-1}
Fundamental	246.6 ± 0.5	245.9		243.1
Overtone	489.0 ± 0.5	488.6	481.6 ± 0.7	482.8
2	728.9 ± 0.7	728.1	718.6 ± 0.8	719.2
3	963.6 ± 1.0	964.3	951.5 ± 1.0	952.2
4	1198.2 ± 1.0	1197.3	1183.7 ± 1.0	1181.8
5	1425.6 ± 1	1427.0		1408.1
6	1653.0 ± 1	1653.6	1630.5 ± 1	1631.0
7	1875.6 ± 1	1876.8		1850.6
8	2098.0 ± 1	2096.9		2066.8

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(2) T. C. Castner and W. Kanzig, *J. Phys. Chem. Solids*, **3**, 178 (1957); C. J. Delbecq, W. Hayes, and P. H. Yuster, *Phys. Rev.*, **121**, 1043 (1961).

(3) M. Hass and D. L. Griscom, *J. Chem. Phys.*, **51**, 5185 (1969).

(4) W. P. Person, *J. Chem. Phys.*, **38**, 109 (1963).

(5) R. E. Minturn, S. Datz, and R. L. Becker, *J. Chem. Phys.*, **44**, 1149 (1966).

(6) D. A. Hatzenbuhler and L. Andrews, *J. Chem. Phys.*, **56**, 3398 (1972).

(7) L. Andrews, *J. Chem. Phys.*, **57**, 51 (1972).

(8) J. E. Cahill and G. E. Leroi, *J. Chem. Phys.*, **57**, 4514 (1969).

(9) W. Holzer, W. F. Murphy, and H. J. Bernstein, *J. Chem. Phys.*, **52**, 399 (1970).

(10) J. C. Evans and G. Y.-S. Lo, *J. Chem. Phys.*, **44**, 3638 (1966).

(11) L. Andrews and J. I. Raymond, *J. Chem. Phys.*, **55**, 3087 (1971).

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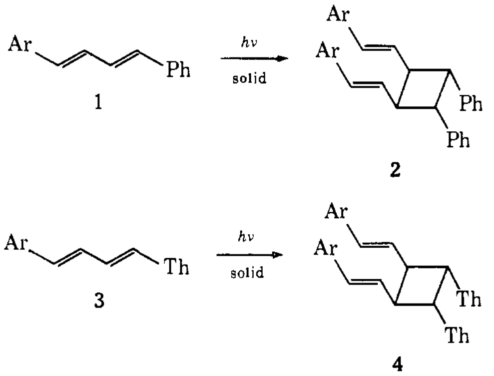
Reactions in Chiral Crystals. Optically Active Heterophotodimer Formation from Chiral Single Crystals

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**.



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]

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(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**.