

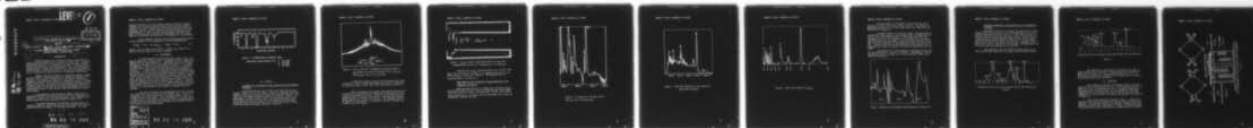
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THE PRODUCTION OF DECARBORANE-14 FROM DIBORANE BY LASER INDUCED--ETC(U)
JUN 78 J A MERRITT, H C MEYER, R I GREENBERG

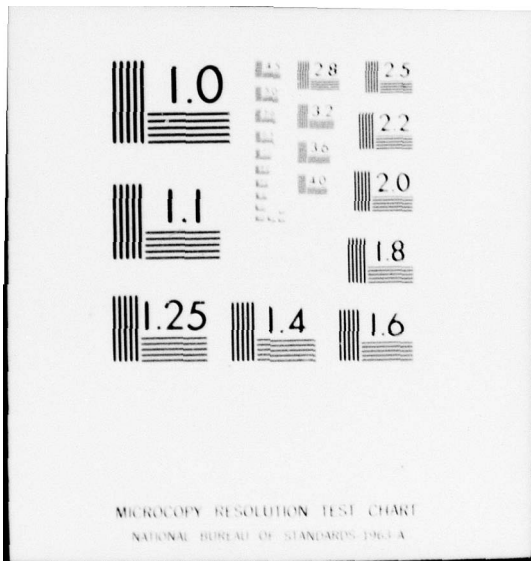
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THE PRODUCTION OF DECBORANE-14 FROM DIBORANE BY LASER INDUCED CHEMISTRY

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JUN 1978
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I. INTRODUCTION

High performance solid propellant fueled rocket motors require burning rate stabilizers to achieve fast burn rates. Presently, n-hexylcarborane (NHC) is considered to be one of the most suitable burning rate modifiers for solid propellant fuels. Its production involves reacting 1-octyne with decaborane-14. The price and quantity limiting factor in the supply of NHC is the lack of an industrial process for synthesizing large quantities of decaborane inexpensively.

Thermal (pyrolysis) methods of influencing chemical processes lead, mainly, to the excitation of all degrees of freedom of the molecule. Both external (translational) and internal (electronic, vibrational, and rotational) degrees of freedom are usually in thermodynamic equilibrium. In addition to there being an unproductive waste of energy, reactions with equilibrium excited molecules characteristically proceed in the direction of breaking the weakest bond, have a considerable percent of back reaction, many side reactions, and produce polymers.

A new approach to the problem of chemical conversions of substances would be to consider the possibility of influencing not a molecule as a whole, but its individual bonds. Such a method of selective excitation can be realized by means of lasers (1-5).

The recent development of high-power infrared lasers has promoted a number of studies dealing with the interaction of this intense radiation with organic and inorganic substrates. The often

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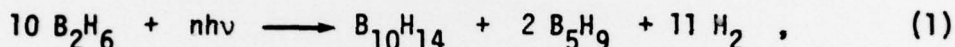
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selective character of the excitation, which can lead to isotope enrichment (6), and other unique features of this new type of photochemistry (7,8) have already been recognized and are attracting considerable interest. Earlier research in this laboratory using laser photochemistry to remove the trace impurity COCl_2 (phosgene) from boron trichloride, BCl_3 photosensitized experiments, etc. (9) encouraged us to investigate the production of decaborane-14 from diborane.

Laser augmented chemistry of the following reaction leading to the production of solid decaborane-14 has been demonstrated:



where $h\nu$ can be either the CO_2 (00^0_1) - (10^0_0), R_{24} , (978 cm^{-1}) or the DF (1-0) P_{12} , (2611 cm^{-1}) laser frequency.

II. EXPERIMENTAL

To avoid handling and storing the usual large (1 lb.) commercial quantities of B_2H_6 we used a 1% gaseous mixture of B_2H_6 in Ar supplied by the Linde Corporation. Immediately prior to irradiation, the B_2H_6 was recovered from Ar by passing the mixture into a condenser cooled to -186°C by an external bath of liquid Ar. A quantity of B_2H_6 sufficient for several irradiations was thus collected as a solid (F. P. = -126°C) while the remaining Ar gas was pumped out of the system. Filling of cells and temporary storage of collected B_2H_6 was facilitated by transferring the B_2H_6 from the condenser to a cold storage bulb by allowing the condenser to warm up to ambient temperature. A cell was then filled by connecting it through a valve and quick disconnect fitting to the vacuum system and adjusting the storage bulb temperature to obtain the desired cell pressure. Typically brass or stainless steel cells 10 cm in length fitted with 3 cm diameter windows of NaCl , KCl , or KBr were used. The infrared spectrum (Figure 1) of the diborane did not reveal the presence of any impurities.

CO_2 laser irradiation was accomplished with both a CW grating tunable laser and a pulsed multigas tunable laser. The DF laser irradiation was accomplished with a 1 kW pulsed chemical laser by "Fresneling off" 10-20 Watts. After irradiation for a given period of time and at varying powers the spectra of static products were obtained using both a Beckman IR5 spectrometer and a DIGILAB FTS-20B Fast Fourier Transform Spectrometer.

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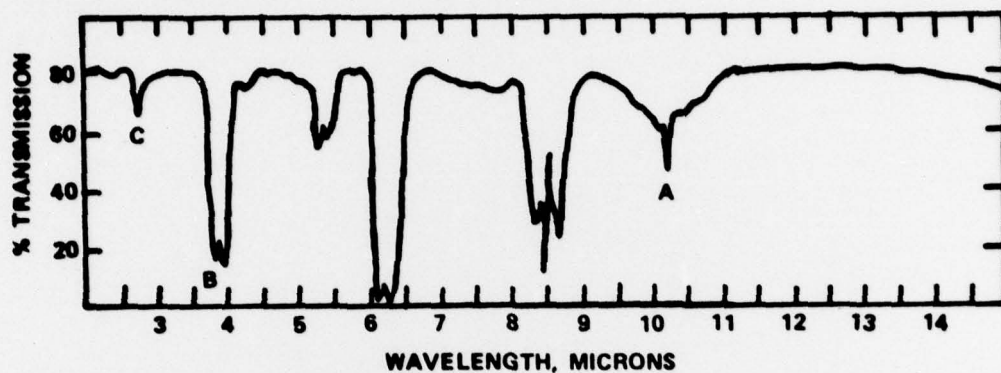


Figure 1. IR SPECTRUM OF GASEOUS B_2H_6

VIBRATIONAL BANDS RESONANT WITH

A:	CO_2 LASER
B:	DF LASER
C:	HF LASER

III. RESULTS

Low Power CO_2 Irradiation of B_2H_6 Resulting in the Formation of $B_{10}H_{14}$

During irradiations with a CW CO_2 laser operating at wavelengths in the 975 cm^{-1} band of B_2H_6 , Figure 2, we observed that white crystals formed along the gas cell walls when the power density of the laser did not exceed a constant threshold of 10 W/cm^2 . Figure 3 is a photograph of crystals formed during a 30 minute irradiation of 400 Torr of B_2H_6 with the R24 laser line, which represents the optimum conditions found within the range of 10 to 800 Torr pressure of B_2H_6 at the attainable wavelengths indicated in Figure 2.

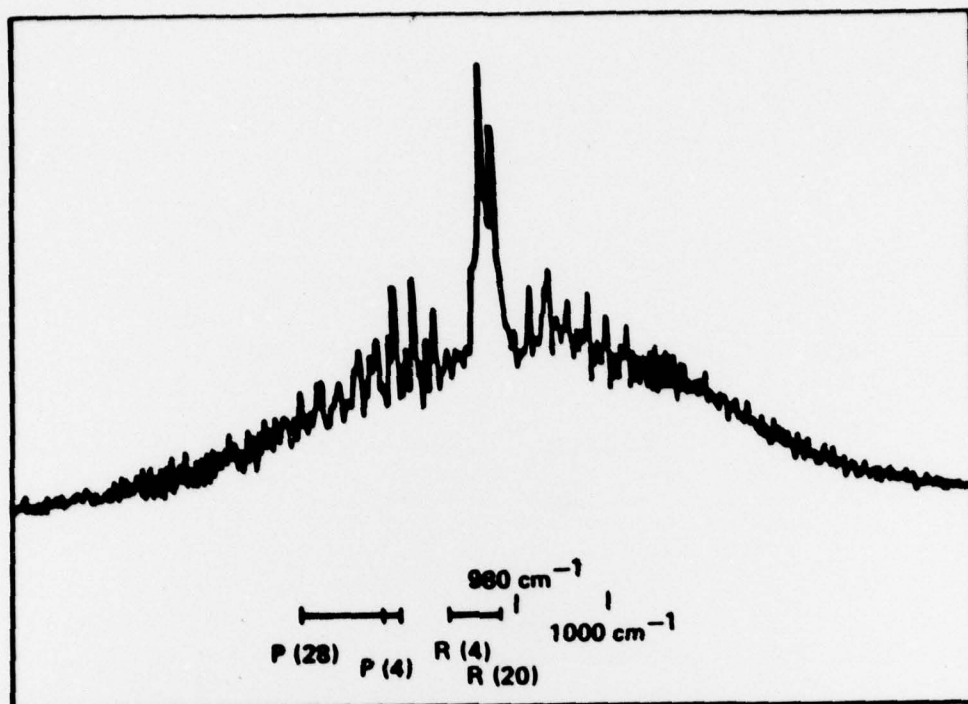


Figure 2. The ν_{14} (975 cm^{-1}) Fundamental Vibrational Band of B_2H_6 Showing the Region Irradiated with the ($\text{P}_{28}\text{-P}_4$) and ($\text{R}_4\text{-R}_{20}$) Lines of the CO_2 Laser.

In addition to white crystals the IR spectrum taken after irradiation, Figure 4 showed the presence of B_5H_9 with characteristic absorption peaks at 900, 1040, 1120, 1400, 1620, and 1800 cm^{-1} .

Prior to analysis, the crystals were removed from the cell by dissolving in MCH (methylcyclohexane) and later recrystallized in a controlled atmosphere dry box. Typically, 10 mg quantities were recovered after a 30 minute irradiation. A melting point determination revealed the crystals melt at 96°C . This together with the IR spectrum of the material in a NUJOL mull (Figure 5) showed the crystals to be pure $\text{B}_{10}\text{H}_{14}$.

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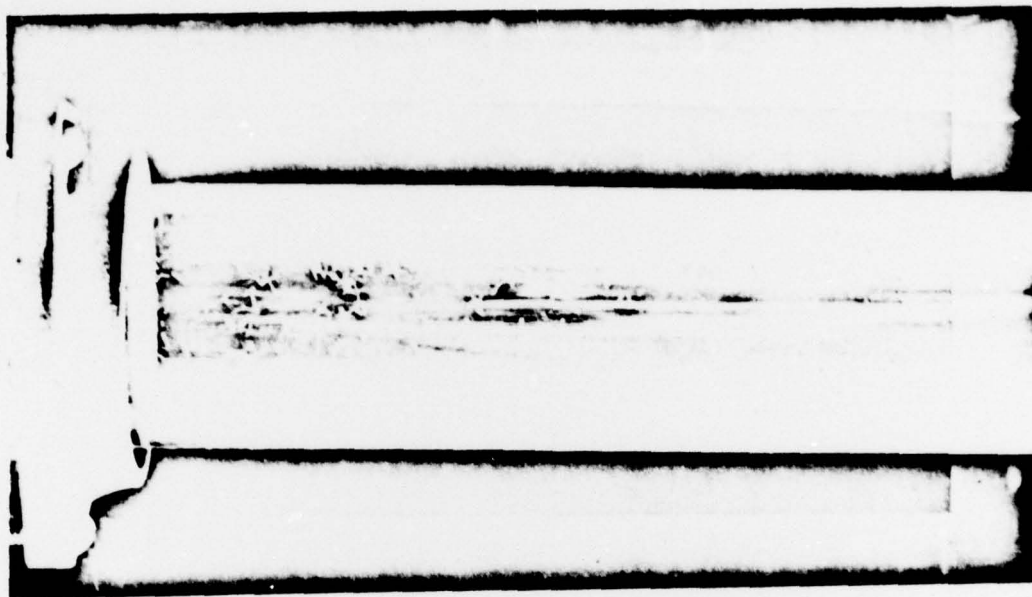


Figure 3. $B_{10}H_{14}$ Crystals Formed when 400 Torr of B_2H_6 was Irradiated with the 975 cm^{-1} Frequency of a 10 W CO_2 Laser.

Characteristic $B_{10}H_{14}$ absorption peaks occur at 1950, 1900, 1520, 1020, and 720 cm^{-1} as shown in an absorption spectrum of commercial $B_{10}H_{14}$ in NUJOL mull, Figure 6. The characteristic BH stretching band is at 2600 cm^{-1} .

High Power CO_2 CW Irradiations of B_2H_6 Resulting in the Formation of Polymers

When the power density of incident laser radiation exceeded 10 W/cm^2 , yellow or white colored particulates were formed immediately upon exposure of B_2H_6 to the radiation. Melting point determination showed the M.P. to exceed 300°C and the powder thus formed was insoluble in pentane and CCl_4 .

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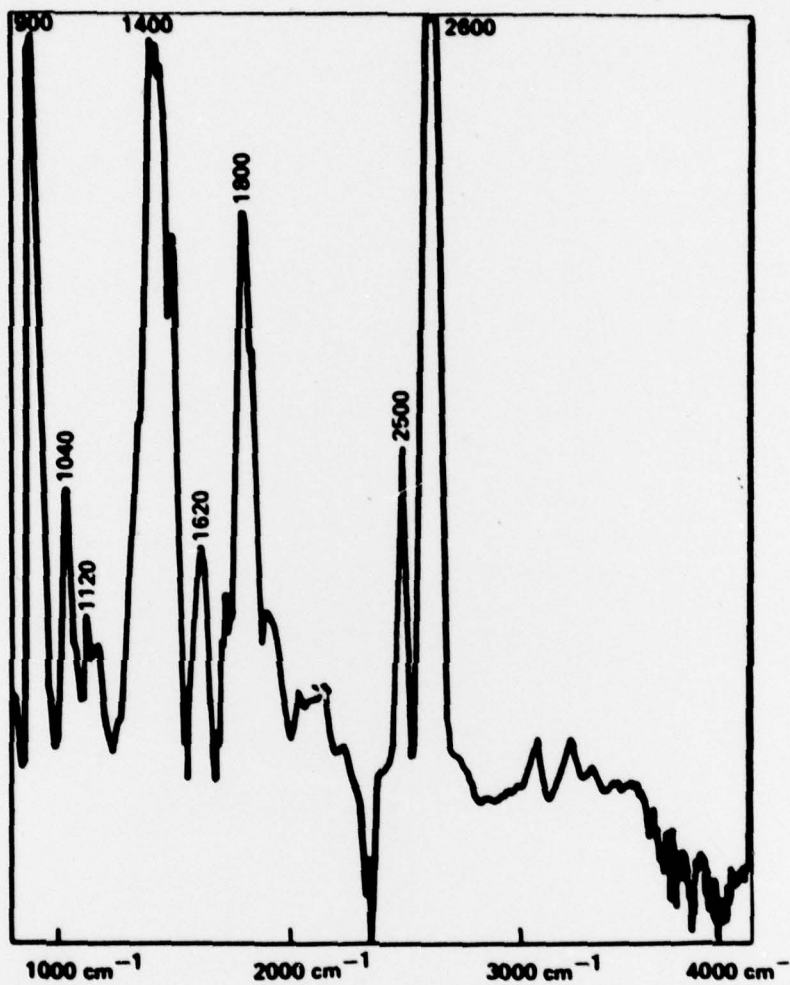


Figure 4. IR Spectrum of the B_5H_9 Product From CO_2 Laser Irradiated B_2H_6 .

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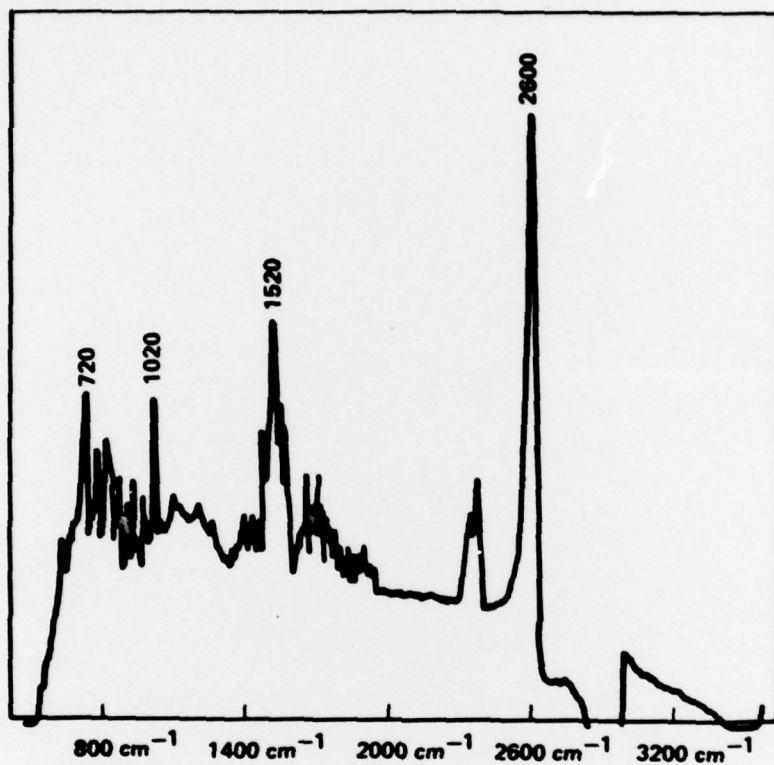


Figure 5. NUJOL Mull Spectrum of the Crystalline White Solid Produced.

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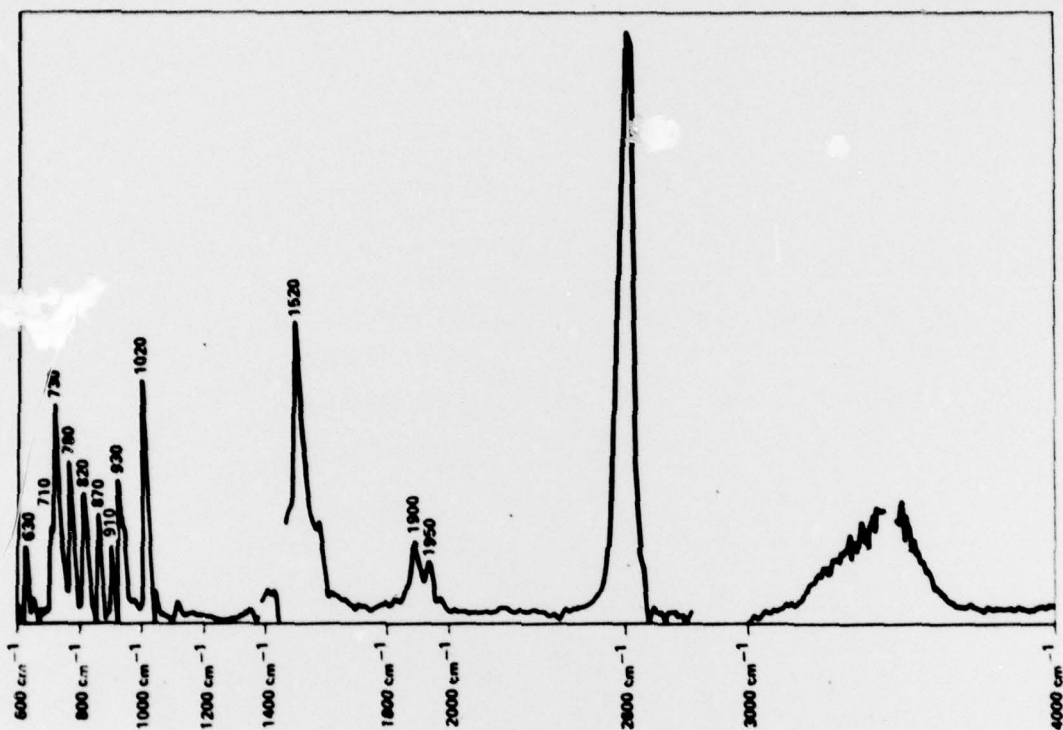


Figure 6. NUJOL Mu11 Spectrum of B₁₀H₁₄.

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Infrared spectra of the powder in KBr pellet gave broad band peaks at 3225, 2525, 1450, 1200 and 875 cm^{-1} . The mineral oil bands were observed at 3210, 2540, 1620, 1490, 1410, 1200, 830, 660, and 550 cm^{-1} , (Figure 7).

A further increase in intensity reaches a threshold where a yellow-white smoke appears at the entrance window and immediately inside it, and a yellow-white powder is deposited on the walls and throughout the cell. The intensity of the threshold for the production of this yellow-white powder is just above the intensity for the most efficient production of the decaborane crystals without the powder. It should be noted that the decaborane crystals are also produced when the powder is produced, but they are contaminated with the powder.

The thresholds for the production of decaborane and the powder were measured as a function of frequency. Measurements from the P20 and P40 to the R34 showed very little variation of these thresholds with frequency.

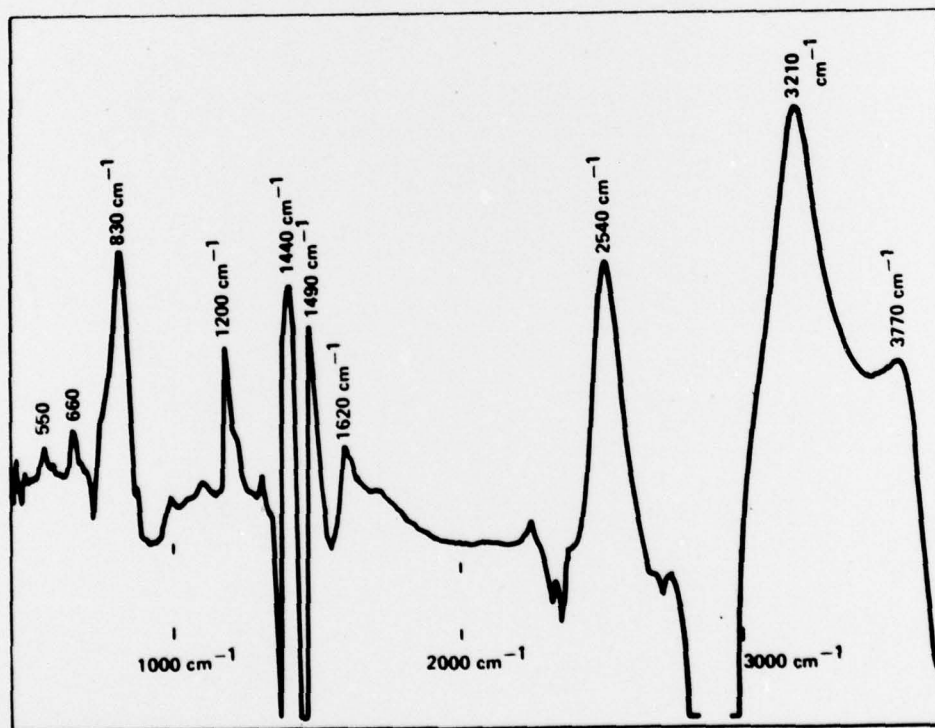


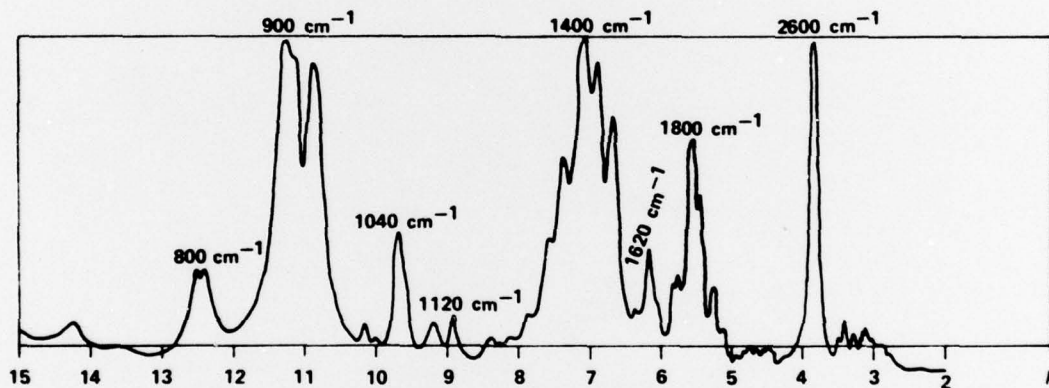
Figure 7. Spectrum of the Polymer Formed Dissolved in Mineral Oil.

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DF Laser Irradiations of B_2H_6 Resulting in the Formation of $B_{10}H_{14}$

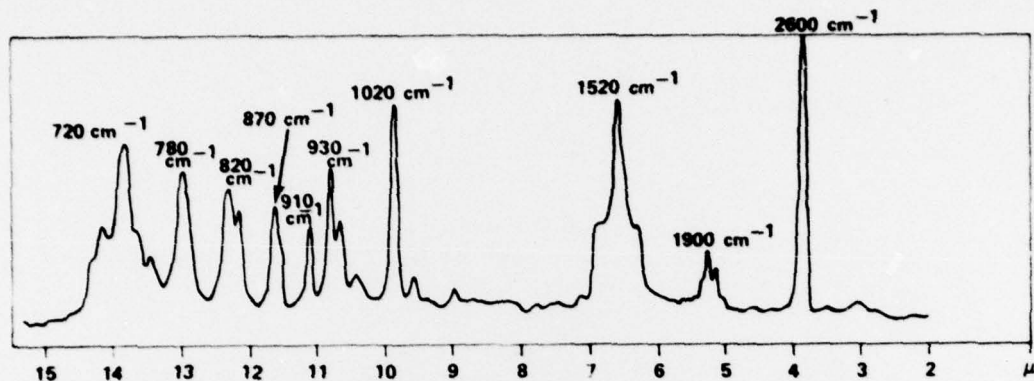
When B_2H_6 (10 Torr in a 10 cm by 3 cm gas cell) was irradiated with the P_{12} (1-0 band) DF laser frequency (2614 cm^{-1}), clear crystals were deposited on the cell walls. The power diverted into the cell from the one kW laser beam was 13 Watts. The DF laser was a large pulsed (13 second duration) chemical laser and the target (cell) was placed some 100 yards from the laser. The laser beam entering the cell was a collimated beam one inch in diameter so that most of the volume of the cell was illuminated. The temperature rise of the cell wall was negligible (less than 5°C).

The spectrum of the cell contents revealed that the products observed were B_5H_9 (gas) and $B_{10}H_{14}$ (solid) (Figures 8 and 9).



LOW RESOLUTION IR SPECTRUM OF THE B_5H_9 PRODUCT FROM DF LASER IRRADIATED B_2H_6

Figure 8



LOW RESOLUTION NUJOL MULL SPECTRUM OF B₁₀H₁₄ PRODUCT FROM DF LASER IRRADIATED B₂H₆

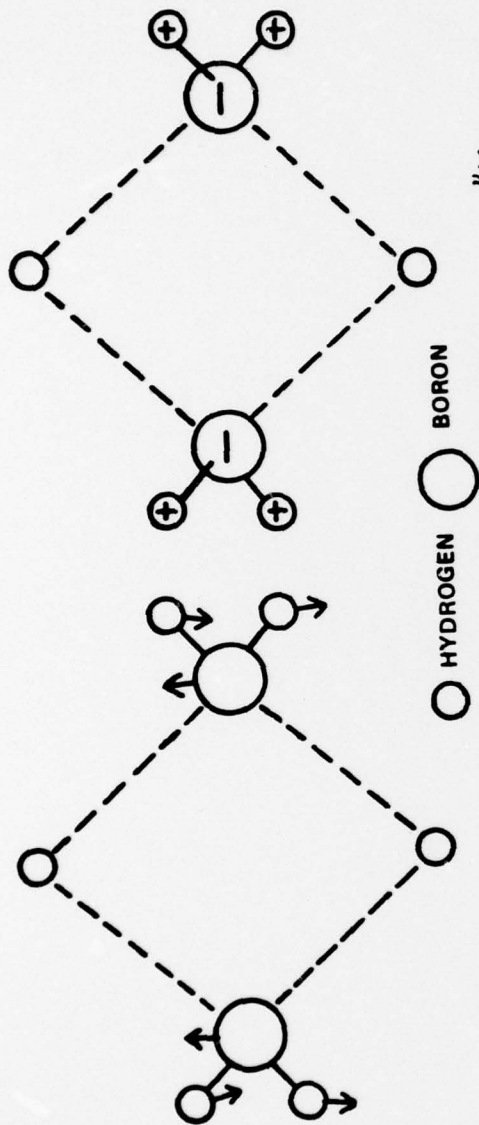
Figure 9

The production of decaborane-14 from diborane by laser induced chemistry (LIC) (Equation 1) represents the first reported example of the synthesis of a large polyatomic molecule by LIC. We were unable to produce any decaborane-14 efficiently and of high purity using pulsed CO₂ laser excitation.

IV. DISCUSSION

From infrared and electron-diffraction evidence, diborane is known to have the bridge structure (10, 11) belonging to the point group D_{2h}, with a four membered B₂H₂ ring in a plane perpendicular to the four terminal hydrogen atoms. The two fundamental vibrational frequencies that are resonant with the CO₂ and DF lasers are shown schematically along with their assignments and measured line positions in Figure 10.

The infrared spectrum of diborane, Figure 1, shows the vibrational bands that are resonant with the CO₂, DF and HF laser frequencies. We have demonstrated the production of decaborane-14 using both the CO₂ and DF laser frequencies. Diborane is mildly endothermic and the bridge bonds' force constant is about one-half as large as



ν_{14}
FUNDAMENTAL MODE
OF B_2H_6
BH₂ WAGGING
978 Cm^{-1}

THE LINE POSITIONS IN THE
PERPENDICULAR-TYPE BANDS OF DIBORANE

K''	2614 Cm^{-1} BAND		974 Cm^{-1} BAND	
	P	R	P	R
0	2614.0		0	
1	2619.0		1	983.9
2	2608.5	2624.5	2	986.9
3	2604.5	2627.8	3	962.7
4	2599.5	2632.0	4	958.1
5	2594.5	2635.5	5	954.1
6	2590.5	2639.5	6	950.0
7	2587.5	2642.3	7	946.0
8	2581.5	2647.5	8	942.0
9	2577.0		9	937.9
10	2573.0		10	933.0
11	2567.0			

ν_8
FUNDAMENTAL MODE OF
 B_2H_6
BH IN-PHASE STRETCHING
2614 Cm^{-1}

SCHEMATIC OF THE FUNDAMENTAL VIBRATION MODES OF B_2H_6
THAT ARE RESONANT WITH THE DF AND CO_2 LASER FREQUENCIES.

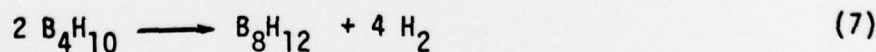
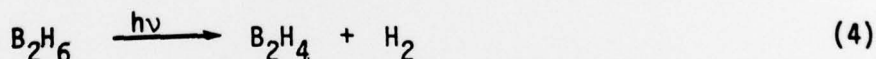
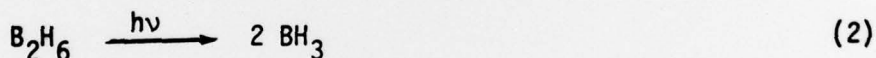
Figure 10

that of the terminal hydrogen bonds. Yet there is substantial evidence that the initial reaction with diborane may be the breaking of the B-H (terminal hydrogen) bond.

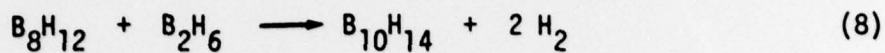
The mercury-photosensitized decomposition of diborane has been explained by postulating B_2H_5 as the primary intermediate, B-H ruptures being common in this type reaction (12). In isotope exchange studies, particularly deuterium, it is always the terminal hydrogen that is exchanged and not the bridged hydrogens. This is especially true for the higher boranes.

Many thermal studies have been conducted on diborane (13,14). The primary intermediate BH_3 has been postulated in these studies to account for B_5H_{11} and other boranes containing odd numbered boron atoms, and the dependency of the rate of product formation common to these reactions being of a one-half or three-halves power of the diborane concentration. However, no direct observance has yet been reported for BH_3 . Another postulated mechanism is the molecular H_2 elimination from B_2H_6 as the primary photodissociation step giving $B_2H_4 + H_2$. Evidence for this consists of the large formation rate of H_2 (greater than the B_2H_5 formation rate) when low pressures of B_2H_6 are pyrolyzed in a hot-cold reactor (the inner cylindrical surface is $1000^\circ C$ while the outer surface is maintained at a much colder temperature), 90% of the product is observed to be B_4H_{10} ($B_2H_6 + B_2H_4$).

Considering the above the following reactions are reasonable:



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V. CONCLUSIONS

↓
Pure $\text{B}_{10}\text{H}_{14}$ can be produced in high yields at room temperature by laser induced chemistry (LIC). No polymer (which is always present in pyrolysis) was observed when we maintained the laser power below a certain threshold (10 W/cm² for the CO₂ laser). Also, the B_5H_9 product is always present in pyrolysis; yet we never observed this product in LIC synthesis. *was*
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This research demonstrates that LIC is a new viable area of chemistry that can be used for cost-effective synthesis of large polyatomic molecules as well as smaller ones. Also, it demonstrates that LIC can be used in a prominent role for the synthesis of high energy binder molecules, burning rate modifiers and fuel additives with a substantial cost-savings (15).
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