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**THE SYNTHESIS AND CHARACTERIZATION OF
4,5-DICYANO OXAZOLE,
A LOW HYDROGEN CONTENT FUEL**

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TECHNICAL REPORT AFRPL-TR-72-68

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FOREWORD

This report summarizes the results of an in-house experimental study, Project 573006CL, conducted from November 1971 to June 1972, to develop a new low hydrogen content fuel. Dr. C. I. Merrill was Project Director and Sgt. R. N. Watson was Project Engineer. The effort was conducted within the Chemistry Branch, Technology Division of the Air Force Rocket Propulsion Laboratory.

This technical report has been reviewed and is approved.

C. E. LUNDBLAD
Acting Chief, Technology Division
Air Force Rocket Propulsion Laboratory

ABSTRACT

Because of a need for a low hydrogen content fuel, 4,5-dicyano oxazole was prepared as a possible candidate for evaluation. Its physical properties were found to be well within defined limits for fuel requirements; however, difficulties inherent in the synthetic process make production of test or operational quantities excessively tedious and costly.

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SECTION I INTRODUCTION

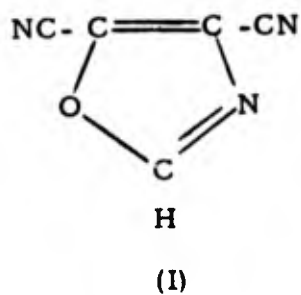
A requirement exists for improved reactant candidates for use in gas dynamic lasers (GDL). Propellants are needed which satisfy the basic composition and flame temperature criteria of the GDL application, and also would be practicable in an operational environment. Additionally, storability, safety and tractability are prime requisites for these reactants. Thus, for consideration as a candidate, the fuel must fulfill the following minimal prerequisites:

1. It should have a carbon-to-hydrogen ratio no greater than 5:1 to achieve desired H_2O concentrations in the combustion products.
2. It should be a liquid at normal ambient temperatures or a relatively low melting solid.
3. It was desirable that the fuel be relatively nontoxic.
4. It was desirable that the fuel be relatively inexpensive.

Previous fuel candidates were found to have serious drawbacks which prevented their utilization as a fuel. Carbon monoxide was too low in energy and presented the difficulty of cryogenic storage in addition to its well-known toxic hazard. Cyanogen also exhibits a high danger of vapor toxicity. A third candidate, 4,5-dicyanofuroxan (DCFO) was synthesized at AFRPL in quantities to be utilized in preliminary combustion studies. With the low vapor pressure of dicyanofuroxan, the vapor toxicity hazard was much reduced. While it was seemingly the most promising of the candidates, DCFO was found to be a detonable material, which eliminated it as a possible candidate fuel.

As an alternative, 4,5-dicyano oxazole (I), was suggested for evaluation as a fuel (Reference 1). The synthesis of this compound was not

reported in the literature, but extrapolation of properties of known oxazole derivatives suggested that the 4,5-dicyano derivative would possess the desired properties. The structure is:



The synthesis of this compound seemed straightforward in view of the fact that requisite starting materials for the dicyano derivative had been previously reported in the literature (Reference 2). The successful synthesis and subsequent characterization of 4,5-dicyano oxazole are presented herein.

The dicyano oxazole was purified further by vacuum sublimation and recrystallization from heptane and was found to have a melting point of 42.5° , a boiling point of about 225° , and the proper elemental analysis: C, 50.41; H, 0.85; N, 35.30 (theoretical); C, 49.60; H, 1.03; N, 34.55 (found). Subsequently, the product was characterized further by infrared, the principal bands being: 3290 (s), 2980 (m), 2260 (m), 1500 (s), 1340 (m), 1230 (s), 1095 (s), 1073 (s), 937 (ms), 887 (m), 637 (m), 621 (m) cm^{-1} . The NMR spectrum consisted of a single signal at 8.16 ppm from tetramethyl silane and the mass spectrum gave the following mass/charge signals and corresponding relative intensities: 119 ($\text{C}_5\text{HN}_3\text{O}^+$, parent, 17.5), 91 (C_4HN_3^+ , 100), 64 (C_3N_2^+ , 31.2), 65 (C_2HN_2^+ , 16.5), 54 (C_2NO^+ , 18.0), 39 (C_2HN^+ , 25.0), 38 (C_2N^+ , 60.0), thus confirming the desired structure.

Two problem areas were manifest in the described synthesis route: (1) consistently low yields (about 4 percent) in the dehydration of the diamide stemming from the coagulation of the reaction mass observed during the distillation, which presumably results in the entrapment and pyrolysis of the product, (2) lower yields observed in the synthesis of the diamide precursors than reported in the literature, particularly in the preparation of diethyl α -oxo- β -hydroxysuccinate.

It was observed that increasing the quantity of the reactants in further attempts at dehydration of 4,5-dicarboxamide oxazole resulted in even lower yields than those observed with smaller quantities. No more than 1.5 to 2.5 grams of 4,5-dicyano oxazole were obtained per run although the quantities of oxazole dicarboxamide employed ranged between 5 and 50 grams. In order to minimize the problem of forming coagulated masses, the reaction was diluted with sand and the apparatus outfitted with a mechanical stirrer. In practice, this technique did tend to minimize the coagulation problem, although the reaction mixture still set up as a hard mass. However, the yields were only slightly improved by the procedure.

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In this system the oxazole structure is produced by heating the appropriate bromo-ketone with formamide. Typically, this reaction proceeded readily by heating a neat, stoichiometric mixture of the reactants to 110° for 30 minutes. Upon isolation of the resulting 4,5-dicarbethoxy oxazole from this reaction, the yields were disappointingly low (15 percent maximum). Continued efforts to improve the results of this reaction by varying conditions resulted in only a minor increase in yield. However, this procedure gave high-purity 4,5-dicyano oxazole in the dehydration reaction, while samples produced by the first reaction sequence were always contaminated with cyanamide.

SECTION III

RESULTS

4, 5-dicyano oxazole (I) was prepared and characterized with the purpose of evaluating it for possible use as a fuel with low hydrogen content. The physical properties exhibited met the prime criteria for a fuel candidate set forth in the introduction (i. e. , acceptable elemental composition, low ambient vapor pressure and low melting point). Problems incurred in efforts to improve yields and scale up the reaction made synthesis of test quantities (100 grams to 1 pound) impractical. Under optimal conditions, the overall yield from the five-step reaction sequence was only 2 to 3 percent.

SECTION IV CONCLUSIONS

Although 4,5-dicyano oxazole exhibits the physical properties desired for a candidate fuel, the difficulties inherent in present methods for its synthesis render the production of test quantities tedious and costly. Because of these factors, 4,5-dicyano oxazole will not be considered as a fuel until significant improvements can be made in its synthesis.

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