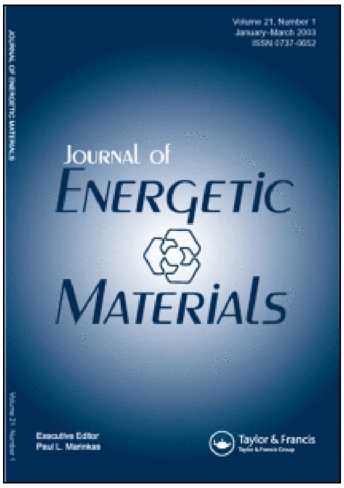

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ISOPHTHALIC DIMETHYLOXAZIRIDINE AS A POTENTIAL BONDING AGENT FOR ROCKET SOLID PROPELLANTS.

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Abstract: The synthesis, reactions and crystal structure of Isophthalic dimethyl oxaziridine are presented here. The synthesis was carried out utilising hydroxylamine-O-sulfonic acid to produce oxaziridine unsubsituted on the nitrogen, which was reacted *in situ* with isophthaloyl dichloride to give the corresponding Isophthatic dimethyl oxaziridine. It is an analogue of Isophthalic 2-methyl aziridine, a product which has been used as a bonding agent for Composite Solid Propellant. The oxaziridine was tested in oxidative reactions of sulfides to sulfoxides, styrene oxide, cyclohexene to cyclohexene oxide, and 1-(2-cyclohexenyl)-2-propanone to [1-(2-cyclohexenyl)-2-propanone] oxide.

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Oxaziridines are three-membered rings constructed of three kinds of atoms having different electronegativities in adjacent positions. Oxaziridines have recently received attention as potential anti-tumor agents and as analogues of penicillin[1]. They also have been considered as potential irreversible alkylating inhibitors of the bacterial serine D,D-transpeptidase[2].

The title compound (1) is expected to be capable of oxidizing sulfides to sulfoxides and epoxidizing alkenes.

Besides being used as an oxidizing agent, the title compound is also envisioned to be a potential bonding agent for Rocket Solid Propellants.

Up to the present, many bonding agents, and their mechanism of action, have been studied. Several papers have been reported as to the action mechanism of bonding agents, and it was pointed out that the bond strength between AP and fuel-binder is dominated by the cohesive strength of binder bulk[3,4] and wetting efficiency of binder prepolymer on AP surface[4,5]. Therefore, of particular interest is the interaction mechanism which bonding agents play in the vicinity of the interface between AP and fuel-binder. Oberth[3] concluded that the bonding agents act by forming a tear-resistant layer around the filler particle, thus preventing peel. Nema[6] described that the bonding agents are either chemically reacting with AP or being absorbed by secondary intermolecular attraction.

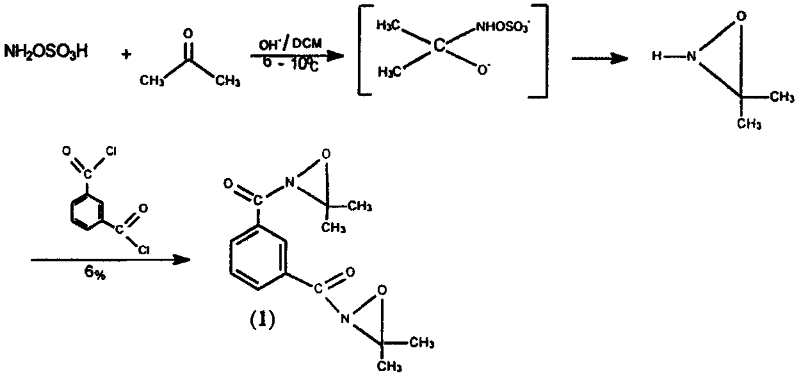
Aziridine derivatives are known as bonding agents which have a high potential for improving the mechanical properties of the propellant grains composed of the fuel-binder, hydroxyl terminated polybutadiene (HTPB), and the solid fillers ammonium perchorate (AP) and aluminium powder[7]. It can be envisaged that certain analogues of these derivatives, such as the oxaziridines, will provide a propellant with higher performance, due to the oxygen in the three membered ring. The oxygen will increase the intermolecular attraction (hydrogen-bonded) between the AP and the bonding agent, improving the mechanical properties of the propellants.

Isophthalic 2-methyl aziridine (**2**), a 3M product known as HX-752, has been successfully tested as a bonding agent for ammonium perchorate in composite solid propellants using hydroxyl terminated polybutadiene. This paper reports to the synthesis of its analogue, the Isophthatic dimethyloxaziridine (**1**), by the replacing of the N-C-C group by N-O-C (**Figure 1**).

FIGURE 1 - Structures of Isophthalic dimethyl oxaziridine (1) and Isophthalic 2-methyl aziridine (**2**).

RESULTS and DISCUSSION

Isophthalic dimethyloxaziridine (**1**) was prepared from the coupling reaction of **3,3-dimethyloxaziridine** with isophthaloyl dichoride (**Scheme 1**).



SCHEME 1 - Syntesis of Isophthalic dimethyloxaziridine

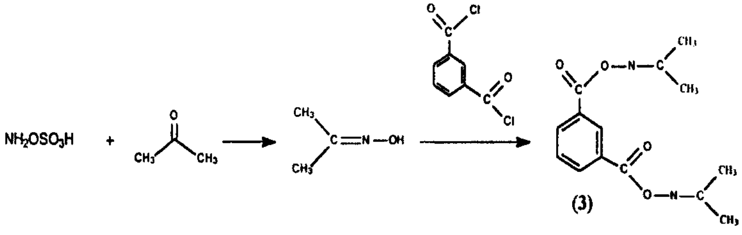
3,3-Dimethyl oxaziridine obtained from hydroxylamine-O-sulfonic acid and acetone, following the method described by Schmitz[8], was not isolated due to its limited stability and it was reacted *in situ* with Isophtahloyl dichloride giving the desired oxaziridine (1) in 6% yield.

The low yield of the oxaziridine (1) is due to the low stability of the unsubstituted oxaziridine (3,3-dimethyl oxaziridine). If the reaction were carried out at 0°C instead of 6°C, the lower temperature will certainly increase the life stability of the intermediate and consequently increase the yield of the product.

In the second step of the reaction where the unsubstituted oxaziridine will react with isophthaloyl dichloride, the HCl formed during the reaction must be neutralized by NaOH present in the mixture reaction, in order to avoid the attack of the HCl to the oxaziridine ring leading to side compounds and lowering the yield. Since oxaziridine is formed *in situ* in an aqueous solution mixed with dichoromethane, and the isophthaloyl dichloride is dissolved in an organic solvente (dichloromethane), the reaction then involves two imiscible solvents. To allow a very good contact among the reagents to gurarantee the efficiency of the reaction, the compounds must be mixed at a very high speed or utilizing ultrasonic stirring. The desired compound will then stay in the organic solvent, and the HCl formed will move to the water solution to be neutralized by NaOH

This new compound was well characterized in the ^1H-NMR by a singlet at 1.61 ppm assigned to be the equivalent methyl groups. The ^{13}C-NMR also showed a typical singlet at 84.5 ppm which is characteristic of the oxaziridine function.

The formation of oxime instead of oxaziridine had to be considered (**Scheme** 2), since the ^1H-NMR, mass spectrum and elemental analysis for compound 1, Isophthatic dimethyloxaziridine and compound 3 (oxime) could be the same. However, the resonance of the C=N group in the ^{13}C-NMR normally appears at 155-165 ppm[9]



(3)

SCHEME 2 - Route to synthesize oxime

Isophthalic dimethyl oxaziridine was isolated as a crystalline solid which recrystallization from ethyl acetate and light petroleum ether (b.p. 60-80°C), gave crystal of suitable quality for a successful X-ray crystallographic structure determination (**Figure** 2).

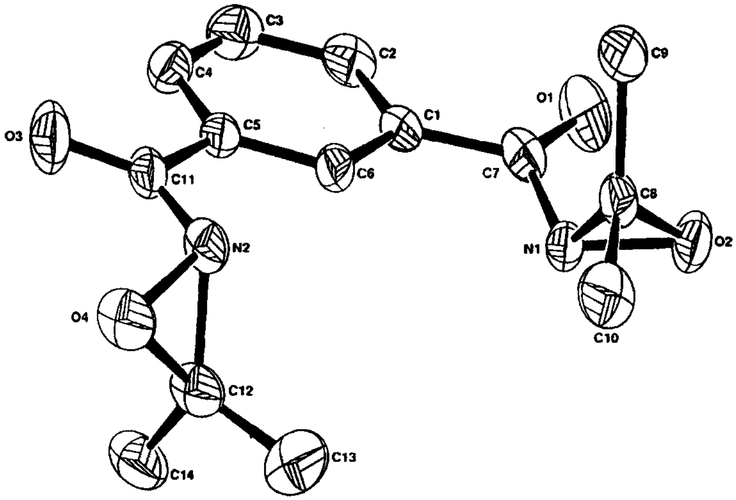


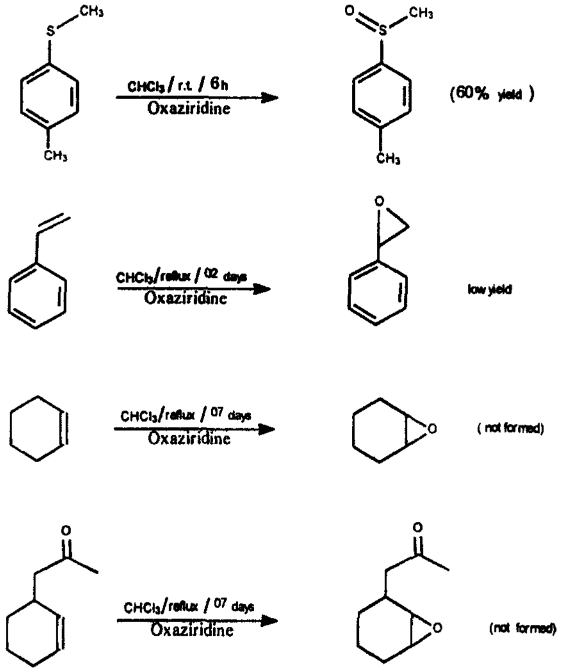
FIGURE 2- X-Ray strucuture of Isophthalic dimethyl oxaziridine

The methyl group from both oxaziridine rings in the compound appeared as only one singlet at 1.65 ppm at ^{1}H-NMR spectrum, and this indicated that the oxaziridine ring is conformationally mobile and can undergo a "flipping" movement that interconverts the nitrogen lone pair from one side of the XYZ plane to the other, thus converting the molecule between its enantiomers faster than the NMR time scale (**Figure 3**).

FIGURE 3- - Flipping movement of nitrogen lone pair

The manufacture of the propellant using Isophthalic dimethyl oxaziridine as a bonding agent for composite solid propellant , is in progress and a comparison of the mechanical properties for propellants manufactured with Isophthalic 2-methyl aziridine (2) and Isophthalic dimethyl oxaziridine will be published later.

The oxaziridine was also tested in the oxidative reactions of sulfides to sulfoxides, styrene to styrene oxide, cyclohexene to cyclohexene oxide and 1-(2-cyclohexenyl)-2-propanone to [1-(-cyclohenenyl)-2-propanone] oxide (**Scheme 3**).



SCHEME 3- Oxidative reactions of the Isophthalic dimethyl oxaziridine

The oxidation of methyl tolyl sulfide proceeded successfully in 60% yield. The ^{1}H-NMR analysis and mass spectrum of the resulting compound confirmed the formation of methyl tolyl sulfide. A strong band at 1039cm^{-1} in the IR spectra also identified the presence of a sulfoxide.

In the epoxidation of styrene only a low yield of styrene oxide was formed when the reaction was refluxed overnight in chloroform, and the reaction failed for the epoxidation of cyclohexene and 1-(2-cyclohexenyl)-2-propanone.

Future studies should possibly address the possibility of developing a catalytic system for oxidation, employing catalytic quantities of oxaziridine (**Figure 4**).

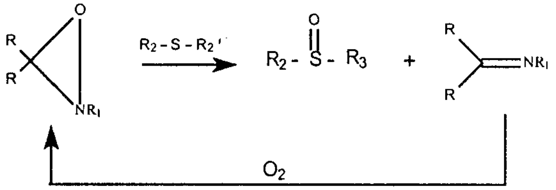


FIGURE 4- - Catalytic Oxidation System for Oxaziridine.

EXPERIMENTAL

Melting points were determined on commercially available apparatus (Electrothermal melting point apparatus), or Büchi 510, and are uncorrected. Elemental microanalysis were carried out using a Carlo Erba 1106 Elemental Analyser. Infrared spectra were recorded in the range of 4000-600cm^{-1}, using a Perkin Elmer 1600 FT-IR spectrophotometer and peaks are reported (v_{max}) in wave numbers (cm^{-1}). Spectra of liquid samples were taken as nujol mulls, or in chloroform solution, as indicated.

Proton NMR (^{1}H-NMR) spectra were recorded on a Jeol GX FT-270 (270 MHz) spectrometer although, where indicated, a Joel GX FT-400

(400 MHz) spectrometer was used. Carbon 13 magnetic resonance (^{13}C-NMR) spectra were recorded on a Jeol GX FT-270 spectrometer operating at 67.8 MHz and using 90 and 135 DEPT pulse sequences to aid multiplicity determination. Chemical shifts (δ) are expressed in parts per million downfield from internal tetramethylsilane (TMS). Mass spectra were recorded using a VG analytical 7070 E instrument with a VG 2000 data system. Electron ionisation (E.I.) was produced using an ionisation potential of 70 eV. Chemical ionistion (C.I.) was empolyed using isobutane as the reagent gas although, where indicated, ammonia was also used.

Isophthalic dimethyl oxaziridine (1). - A solution of hydroxylamine-O-sulfonic acid (0.01mol, 1.12g) in water (10ml) and NaOH 2N (5ml), was added rapidly to a stirred solution of acetone (13.6mmol, 1.0ml) in dichloromethane (30ml) and NaOH 2N (20ml) at 2-5°C. Immediately, a solution of isophathaloyl dichloride (0.005mol, 1.0g) in dichloromethane (10ml) was added, and the stirring was continued for an additional 10 min. The dichloromethane layer was then separated and dried over magnesium sulphate and filtered. Concentration on a rotating evaporator gave a white solid wich was recrystallised from ethyl acetate/light petroleum (b.p. 60-80°C) to give colourless crystals (0,16g, 6.0% yield): m.p. 114-116°C; R_f = 0.27(petrol-ethyl acetate 4:1); ν_{max}($CDCl_3$)/cm^{-1} 1716(C=O), 1432(oxaz.), 1200(P=O); δ_H($CDCl_3$) 1.65(s, $C\underline{H}_3$), 7.66-8.61(m, Ar-$\underline{H}$); δ_C($CDCl_3$) 22.14(s, C-$\underline{C}H_3$), 85.12(s, C_{oxaz}.), 128.97, 129.54, 132.07, 133.58(4s, Ar). 176.56(s, C=O); *m/z*(C.I.) 277(MH^+, 25%); *m/z*(E.I.) 276(M^+, 2%), 240(M^+ - $NOC(CH_3)_2$, 90), 146(62), 118(100), 90(78), 43(66). Anal. Calcd. for $C_{14}H_{16}N_2O_4$: C, 60.8, H, 5.8; N, 10.1:;Found: C, 60.6, H, 5.8; N, 10.0.

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