

# ***Hydrogen Bonding of 2,4-Dinitrotoluene to Unesterified Hydroxyl Groups in Nitrocellulose***

## **INTRODUCTION**

Deterrents are compounds utilized to moderate the burning rates of small arms propellants early in the interior ballistic cycle. In the case of extruded propellants, deterrents are coated on the outer surface of the cylinders as well as on the interior surface of an axial perforation, which is sometimes present. This study is concerned with the use of dinitrotoluene (DNT) solely as a deterrent material. Crude DNT utilized for the process is a mixture of various isomers, with 2,4-DNT predominating. For this reason, purified 2,4-DNT was incorporated into nitrocellulose (NC) cast films and studied by means of infrared spectroscopy. Past studies<sup>1,2</sup> have shown that deterrents utilized for spherical NC small arms propellants hydrogen bond to unesterified hydroxyl groups present in NC, and that this interaction is responsible for the deterrent concentration profile.

The purpose of the present study was to investigate the possibility of a similar interaction with 2,4-DNT.

## **EXPERIMENTAL**

NC (12.6% N) with a weight average molecular weight of 139,600, and a number average weight of 90,450, was utilized for this study. A standard solution of NC was prepared by dissolving 0.84 g in 100 mL of reagent grade ethyl acetate (EA).

Crude DNT, representative of that utilized for propellant manufacture, was recrystallized from EA and the purified compound was found to be the 2,4 isomer with a melting point of 69–70.5°C. A standard solution of the 2,4-DNT was prepared by dissolving 0.154 g in 100 mL of reagent grade EA.

Samples for infrared study were prepared by mixing 1 mL of the NC solution with 1 mL of the 2,4-DNT solution and casting on sodium chloride plates. Cast films were subjected to a roughing pump vacuum for 16–20 hr in order to remove traces of the solvent.

Spectra were taken on a Perkin-Elmer spectrophotometer (model 283B). The NO<sub>2</sub> stretching region was examined by means of the 5× abscissa expansion.

## **DISCUSSION**

Purified 2,4-DNT was incorporated into cast films of NC and studied by means of infrared spectroscopy. A shift in the NC hydroxyl stretching frequency was observed when 2,4-DNT was present in the cast film. The free  $\nu$ -OH of the NC appeared at 3558 cm<sup>-1</sup>, while the  $\nu$ -OH measured with the 2,4-DNT present in the film shifted to 3542 cm<sup>-1</sup>. This shift in  $\nu$ -OH of 16 cm<sup>-1</sup> indicates that weak hydrogen bonding had occurred between the unesterified hydroxyl groups in NC and the nitro groups of 2,4-DNT.

Examination of the 2,4-DNT spectra in the NO<sub>2</sub> stretch region indicated that the symmetric NO<sub>2</sub> stretch occurred at 1342 cm<sup>-1</sup>, while the asymmetric stretch occurred at 1524 cm<sup>-1</sup>. Both the NO<sub>2</sub> stretching peaks were broad. When the DNT was present in the NC cast film, the NO<sub>2</sub> asymmetric stretching frequency shifted to 1532 cm<sup>-1</sup> and the symmetric NO<sub>2</sub> stretching frequency shifted to 1346 cm<sup>-1</sup>. With the shifts, both peaks became considerably narrower. Franck, Hormann, and Scheibe<sup>3</sup> have reported that when the nitro group is shifted out of the plane of the ring, as would be expected with a bulky group in the ortho position, the asymmetric NO<sub>2</sub> stretching frequency shifts to higher frequencies in the range of 1565–1540 cm<sup>-1</sup>. In the present case, the asymmetric NO<sub>2</sub> stretching frequency shifted to a higher frequency but not into the 1565–1540 cm<sup>-1</sup> region. This could be accounted for by a small off-setting shift due to the hydrogen bonding between the NO<sub>2</sub> groups and unesterified hydroxyl groups in NC. Although the previous study did not comment on the symmetric NO<sub>2</sub> stretching frequency, a similar shift would seem reasonable. Bellamy<sup>4</sup> has reported that marked alterations occur in the band shape of both NO<sub>2</sub> absorptions when steric hindrance is present. A specific example, given by Bellamy, is a comparison of the half-band widths

of *o*-nitrotoluene and *p*-nitrotoluene. In *o*-nitrotoluene the half-bandwidth of the symmetric NO<sub>2</sub> absorption is twice that of the corresponding band in *p*-nitrotoluene. In the present study, both the symmetric and asymmetric DNT NO<sub>2</sub> stretching frequencies fell to about one-half the half-bandwidth when hydrogen bonding occurred.

Based on the shifts in stretching frequencies and changes in band widths, it appears that hydrogen bonding has occurred between unesterified hydroxyl groups in NC and the NO<sub>2</sub> groups of DNT. Further, this interaction has resulted in the NO<sub>2</sub> present in the two position being raised out of the plane of the aromatic ring.

#### References

1. B. W. Brodman, M. P. Devine, and M. T. Gurbarg, *J. Appl. Polym. Sci.*, **18**, 943 (1974).
2. B. W. Brodman, J. A. Sipia, Jr., and S. Schwartz, *J. Appl. Polym. Sci.*, **19**, 1905 (1975).
3. Franck, Hormann, and Scheibe, *Chem. Ber.*, **90**, 330 (1957) cited in L. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958, p. 301.
4. L. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958, p. 303.

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