

Notes

Hydrogen Bonding of Dinitrotoluene Isomers to Unesterified Hydroxyl Groups in Nitrocellulose

INTRODUCTION

2,4-Dinitrotoluene belongs to a class of compounds called deterrents. These compounds are used to moderate the burning behavior of nitrocellulose-based propellant grains early in the ballistic cycle when the total bed surface area is at maximum. In the case of spherical military propellant grains, di-*n*-butyl phthalate (DBP) is diffused some distance into the propellant grain in order to gain initial burning rate control. An experimental study has resulted in the establishment of the DBP concentration profile¹ in spherical propellant. Further, a previous study established that a diffusion with interaction mechanism was responsible for this profile and formulated a model which is capable of predicting the depth of penetration of DBP into a spherical propellant grain.² Past work has also shown that the experimental measured concentration profile was due to hydrogen bonding between a DBP carbonyl group and unesterified hydroxyl groups in nitrocellulose.³

In cylindrical nitrocellulose-based military propellants, 2,4-dinitrotoluene (2,4-DNT) is used as a deterrent material. A recent study has established that hydrogen bonding occurred between the nitro group of 2,4-dinitrotoluene and unesterified hydroxyl groups in nitrocellulose.⁴ Since the 2,4-dinitrotoluene used for deterring propellant is not totally purified, it was decided to study the hydrogen bonding properties of the various isomers since their presence influenced the deterrent concentration profile and the ultimate burning characteristics of the propellant.

DISCUSSION

The various isomers of dinitrotoluene were incorporated into cast films of nitrocellulose and studied by means of infrared spectroscopy. Both the hydroxyl stretching region and the symmetric and asymmetric nitro stretching regions were examined, in order to characterize the hydrogen bonding properties. Table I is a listing of the specific isomers along with the γ -OH, measured when they were incorporated into nitrocellulose films, as well as the shift in γ -OH obtained with each isomer. It is interesting to note that the specific isomer used for deterring (2,4-DNT) formed a somewhat weaker hydrogen bond than did the 2,3, 2,5, and 3,4 isomers. A stronger hydrogen bond is more desirable in terms of long-term storage stability.

Table II is a listing of the nitro stretching frequencies for each compound along with those obtained on hydrogen bonding.

TABLE I
Shift in Nitrocellulose Hydroxyl Stretching Frequency for the Isomers of DNT

Compound	γ -OH cm^{-1}	$\Delta\gamma$ -OH cm^{-1} *
2,3-DNT	3530	37
2,4-DNT	3540	27
2,5-DNT	3530	37
2,6-DNT	3545	22
3,4-DNT	3530	37
3,5-DNT	3550	16

* (γ -OH nitrocellulose) - (γ -OH nitrocellulose on hydrogen bonding with the isomer). The γ -OH for nitrocellulose was 3567 cm^{-1} .

TABLE II
Symmetric and Asymmetric NO₂ Stretching for the Various Isomers and NC Cast Films of the Isomers

Isomer of dinitrotoluene (DNT)	NO ₂ asymmetric (cm ⁻¹)	NO ₂ Symmetric (cm ⁻¹)	NO ₂ asymmetric in cast NC films (cm ⁻¹)	NO ₂ symmetric in cast NC film (cm ⁻¹)
2,3-DNT	1543	1341	1535	1346
2,4-DNT	1520	1345	1535	1347
2,5-DNT	1550	1345	1537	1345
2,6-DNT	1524	1348	1535	1346
3,4-DNT	1520	1345	1537	1348
3,5-DNT	1532	1336	1537	1345

Examination of Table II indicates shifts in the asymmetric stretching frequencies for all isomers studied. The interesting point is that all isomers essentially shifted to the same frequency (1535–1537 cm⁻¹) on hydrogen bonding. This is interesting in view of the diversity of inductive, resonance, and steric effects exhibited by the various isomers. In all cases the half-bandwidth of both the symmetric and asymmetric nitrostretching peaks narrowed to about one half the half-bandwidth when hydrogen bonding occurred. Bellamy⁵ has reported that marked alterations occur in bandwidth when the nitro group is subjected to steric hindrance. The case of ortho- and paranitrotoluene were cited as an example. For orthonitrotoluene the half-bandwidth is a little more than twice that of *p*-nitrotoluene. When hydrogen bonding occurred with the DNT isomers, both the symmetric and asymmetric stretching peaks narrowed considerably. This might indicate that the nitro group was lifted out of the plane of the aromatic ring when hydrogen bonding occurred. Further, in most cases a peak at about 1600 cm⁻¹ was present in the isomers. This peak has been identified as being indicative of an aromatic structure.⁵ When hydrogen bonding occurred between the various isomers and nitrocellulose, the peak at 1600 cm⁻¹ disappeared. It should be pointed out that the 1600 cm⁻¹ is usually associated with a peak at 1580 ± 20 cm⁻¹. In our work this peak sometimes appeared as a shoulder on the rather wide asymmetric nitro stretching frequency. It, therefore, appears that hydrogen bonding of DNT isomers to nitrocellulose results in the lifting of the nitro group out of the plane of the aromatic ring with the possible alteration of the aromatic character of the compound. These facts could account for the fact that the asymmetric nitro stretching frequency for the various isomers reached a constant on hydrogen bond formation.

EXPERIMENTAL

NC (12.6%N) with a weight average molecular weight of 139,600 and a number average molecular weight of 90,450 was utilized in this study. Nitrogen content and molecular weight data were measured at the time the nitrocellulose was isolated. A standard solution was prepared by dissolving 0.42 g of NC in 100 mL of reagent grade ethyl acetate.

Samples for infrared study were prepared by mixing sufficient NC solution with a known amount of the DNT isomer such that there were 1.2 molecules of the isomer per free unesterified hydroxyl group in the nitrocellulose. The resulting solutions were cast on NaCl plates and dried under vacuum, at 40°C for a minimum of 48 h.

Infrared spectra of the isomers were obtained as Fluorolube mulls.

Spectra were taken on a Perkin-Elmer Spectrophotometer (Model 283B).

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