the values of $\sigma$ were 2–3 times those given in Table IV. This result is not surprising if we consider Figures 2 and 3 showing activity coefficients with maximum and minimum as a function of composition, particularly for the system 1,3-dioxolane–cyclohexanol. Moreover, both systems have activity coefficients up to 2.5 and present, for a wide composition range, deviations from the Raoult law which are positive for 1,3-dioxolane ($\gamma_1 >$ 1) and negative for the six-membered cyclic compounds ($\gamma_2 <$ 1).

**Registry No.** 1,3-Dioxolane, 646-06-0; cyclohexanone, 108-94-1; cyclohexanol, 108-93-0.

## Literature Cited

(1) Francesconi, R.; Castellari, C.; Arcelli, A.; Comelli, F. *Can. J. Chem. Eng.* **1980**, *58*, 1113.
(2) Comelli, F.; Castellari, C.; Francesconi, R. *J. Chem. Eng. Data* **1981**, *26*, 334.
(3) Francesconi, R.; Comelli, F.; Castellari, C. *J. Chem. Eng. Data* **1982**, *27*, 53.
(4) Castellari, C.; Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1982**, *27*, 156.
(5) Castellari, C.; Comelli, F.; Francesconi, R., submitted to *J. Chem. Eng. Data*.
(6) Sawitowski, H.; Pillavakis, A. P. *J. Chem. Eng. Data* **1982**, *27*, 64.
(7) Carrà, S.; Ragaini, V.; Zanderighi, L. "Operazioni di Trasferimento di Massa", 1st ed.; Manfredi: Milano, 1969.
(8) Castellari, C.; Francesconi, R.; Bubani, B.; Comelli, F. *Can. J. Chem. Eng.* **1983**, *61*, 246.
(9) Nelder, J. A.; Mead, R. *Comput. J.* **1965**, *7*, 308.
(10) Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163.
(11) Green, J. R.; Margerison, D. "Statistical Treatment of Experimental Data", 1st ed.; Elsevier: New York, 1977.
(12) Eadie, W. T.; Dryard, D.; James, F. E.; Roos, M.; Sadoulet, B. "Statistical Methods in Experimental Physics"; 1st ed.; North-Holland: Amsterdam, 1971.

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# NEW COMPOUNDS

# Synthesis and High-Resolution Mass-Spectral Analysis of Isotopically Labeled 2,4,6-Trinitrotoluene

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**The high-resolution electron impact spectra of 2,4,6-trinitrotoluene (TNT) and its $^2H$ and $^{15}N$ isotopic derivatives have been determined. 2,4,6-Trinitrotoluene loses an OH group to form the major ion, *m/e* 210, which undergoes various fragmentation reactions. The parent ion of 2,4,6-trinitrotoluene, *m/e* 227, loses three $NO_2$ groups to form the second most abundant ion, $C_7H_5^+$, which then rearranges to form a tropylium-like ion. The $C_7H_5^+$ species then undergoes loss of $C_2H_2$ to form $C_5H_3^+$, in a manner similar to tropylium.**

## Introduction

In previous years, this laboratory has undertaken various studies (*1–3*) to determine the mechanism of the thermochemical decomposition reactions of 2,4,6-trinitrotoluene (TNT). Recently, we reported the results of quantum-mechanical calculations and X-ray crystallographic studies of TNT (*4*). This latter investigation established that TNT exists in two different forms within the unit cell, and both forms are stabilized by extensive hydrogen bonding. With the above in mind, we have synthesized several $^{15}N$ and $^2H$ isotopic versions of TNT, to observe the effects of such substitution on the mass-spectral degradation of TNT.

## Experimental Section

***Instrumentation.*** All high-resolution mass spectra reported herein were obtained with a Kratos MS-50 double-focusing mass spectrometer operating at 70 eV with a resolution of 180 000 (10% valley), coupled to an INCOS data system. Samples were introduced via the direct insertion probe at ambient temperature. The source temperature was set at 250 °C for the measurement of normal spectra. Metastables were observed in the second field-free region between the electrostatic analyzer and magnet and were recorded with a light beam oscillographic recorder. Fragmentation pathways were confirmed by using mass-analyzed kinetic energy spectrometry (MIKES) and helium collisionally activated MIKES.

$^1H$ NMR spectra were obtained with a Varian T-60A spectrometer operating at ambient temperature. The melting points were determined with a Reichert micro hot stage melting point apparatus equipped with a calibrated thermometer.

***Synthesis of TNT.*** This was synthesized by using a modified version of a previous method (*5*). A 75-mL sample of fuming sulfuric acid (15% oleum) was cooled to 0 °C, and 27 mL of 90% nitric acid was added dropwise. This mixed acid solution was warmed to room temperature and 35.4 g of 2,4-dinitrotoluene was added. Gentle stirring was started and continued from this point on. The temperature was slowly raised to 90 °C (60 min), at which point the resulting exothermic reaction required cooling to keep the temperature below 120 °C. The reaction was maintained at 90–100 °C for the next 2 h. The reaction was then cooled and allowed to stand overnight at 25 °C. The resulting mixture was then extracted with 800 mL of methylene chloride. The methylene chloride layer was neutralized with 500 mL of saturated sodium carbonate solution and washed twice with 500 mL of distilled water. The methylene chloride was removed with a roto-vac, and the solid TNT recrystallized from ethanol and $CCl_4$; 27.2 g of product (mp 81.5–82.0 °C) was obtained (62% yield).

***Synthesis of $\alpha$-$d_3$-TNT.*** This was synthesized by a modified version of a previous method (*1*) as follows: A solution was prepared containing 0.5 g of TNT, 15 mL of $(CD_3)_2CO$, 6 mL of $CH_3OD$, and 3 mL of $D_2O$; 0.1 mL of triethylamine was added to the above solution and the mixture at room temperature for

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90 min. DCl was then added until the pD was lowered to 3. The solution was again stirred for 1 h and the TNT-$d_3$ extracted with 50 mL of $CHCl_3$. The $CHCl_3$ was evaporated and the solid recrystallized first from ethanol–water (2:1) and then from $CCl_4$; 0.32 g of product (mp 81.5–82.0 °C) was obtained with greater than 99% deuterium enrichment (63% yield).

***Synthesis of (4-$^{15}NO_2$)-TNT.*** A 6-g sample of fuming sulfuric acid (15% oleum) was cooled to 0 °C, and 1.0 g of 100% $H^{15}NO_3$ (KOR, Inc., Cambridge, MA) was added dropwise. This mixed acid solution was warmed to room temperature and 1.0 g of 2,4-dinitrotoluene was added with gentle stirring from this point on. The temperature was then raised slowly to 90 °C (60 min), and the reaction maintained at 90–100 °C for 2 h. The reaction was cooled overnight at 25 °C, and the resulting mixture extracted twice with 10 mL of methylene chloride. The 20-mL extract was then washed once with 15 mL of saturated $NaHCO_3$ solution and once with 20 mL of distilled water. The methylene chloride was removed by evaporation with compressed air and the resulting solid recrystallized from $CCl_4$; 0.742 g of product (mp 81.5–82.0 °C) was obtained with greater than 99% $^{15}N$ enrichment (59% yield).

***Synthesis of (2,6-$^{15}NO_2$)-TNT.*** A 1-g sample of 4-nitrotoluene (recrystallized from 50:50 ethanol–water) was added to 3 g of previously cooled concentrated $H_2SO_4$; 2 g of 50% (w/w) $H^{15}NO_3$ (Stohler Isotope Chemicals, Waltham, MA) was added dropwise with gentle stirring from this point on; 3 mL of fuming sulfuric acid (15% oleum) was added dropwise and the mixture slowly heated (1 h) to 100 °C. The reaction was maintained at 100 °C for 3 h and then cooled overnight at 25 °C. The resulting reaction mixture was further cooled to 0 °C, and 5 mL of fuming sulfuric acid (15% oleum) was added; 1.0 g of 100% $H^{15}NO_3$ was then added dropwise, and the mixture heated to 100 °C for 3 h as before. The reaction mixture was allowed to cool overnight at 25 °C. The labeled TNT was twice extracted from the reaction mixture by using 20 mL of methylene chloride each time. The 40 mL of extract was washed once with 30 mL of saturated $NaHCO_3$ solution and twice with 40 mL of distilled water. The methylene chloride was evaporated with compressed air, and the remaining solid twice recrystallized from ethanol; 0.700 g of product (mp 81.5–82.0 °C) was obtained with greater than 99% $^{15}N$ enrichment (42% yield).

***Synthesis of (2,4,6-$^{15}NO_2$)-TNT.*** Toluene (1.0 g) was added to 3.0 g of concentrated $H_2SO_4$ at 0 °C, and 2.0 g of 50% $H^{15}NO_3$ added dropwise. The solution was heated to approximately 35 °C for 6 h and allowed to cool overnight. The spent acid (lower) layer was then drawn off and the reaction mixture cooled to 0 °C. The following were added sequentially while the mixture was kept at 0 °C: 5.6 g of concentrated $H_2SO_4$, 2.0 g of 50% $H^{15}NO_3$, and 9.5 g of fuming sulfuric acid (15% oleum). The reaction mixture was then stirred and heated to 90 °C for approximately 8 h, after which it was allowed to cool overnight. The reaction mixture was again cooled to 0 °C, and 15 g of fuming sulfuric acid (15% oleum) and 1.0 g of 100% $H^{15}NO_3$ were added sequentially. The mixture was stirred and heated to approximately 95 °C for 6 h and allowed to cool overnight. The product was extracted twice with 25 mL of methylene chloride, and any acid carried over into the extract was eliminated by washing with 50 mL of saturated $NaHCO_3$ solution, and twice with 40 mL of $H_2O$. The methylene chloride solution was then evaporated and the product recrystallized from ethanol (mp 81.5–82.0 °C); 0.65 g of product was obtained with greater than 99% $^{15}N$ enrichment (26% yield).

***Synthesis of α-$d_3$-(2,4,6-$^{15}NO_2$)-TNT.*** This compound was prepared by deuterating (2,4,6-$^{15}NO_2$)-TNT as described above.

***$^1H$ NMR of Isotopically Labeled TNT's.*** All NMR spectra were obtained in $C_6D_6$ with tetramethylsilane ($Me_4Si$) as an internal standard. The methyl singlets were centered at δ 1.90 (TNT), 1.87 ((4-$^{15}NO_2$)-TNT), 1.89 ((2,6-$^{15}NO_2$)-TNT), and 1.87 ((2,4,6-$^{15}NO_2$)-TNT). The aromatic protons were centered at δ 7.87 (TNT), 7.80 (α-$d_3$-TNT), 7.84 (doublet, $J_{NA}$ = 1.6 Hz; (4-$^{15}NO_2$)-TNT), 7.84 ((2,6-$^{15}NO_2$)-TNT), 7.82 ((2,4,6-$^{15}NO_2$)-TNT), 7.79 (two triplets, $J_{NH}$(ortho N) = 2.0 Hz, $J_{NH}$(para N) = 1.0 Hz, α-$d_3$-(2,4,6-$^{15}NO_2$)-TNT). All δ's are given in ppm relative to $Me_4Si$.

## Results and Discussion

The relative abundances from the 70-eV spectra of the various isotopomers of TNT are given in Table I. Only those abundances greater than 1% are reported. The parent ion is observed at values less than 1% for every TNT isotopic derivative. In all cases, the major ion is the $C_7H_4N_3O_5$ species, as determined by measurements to within 0.1 mmu. The isotopic versions of TNT confirm that this species is formed by the loss of O from an *o*-nitro group and an H from the methyl group as previously postulated (*6*). The accuracy of the measurements is reflected in the appearance of several molecular species at a particular *m/e* value given in Table I. Typical results of exact mass measurements vs. the calculated mass values are contained in Table II. The average deviation for the observed mass-calculated mass value given in Table II is less than 0.2 mmu, exclusive of the last two species, *m/e* 63 and 62.

The initial loss of OH from $(TNT)^+$ to form the *m/e* 210 species is supported by the presence of a metastable ($m^*$) peak at *m/e* 194.3. Similar results were obtained for *o*-nitrotoluene (*7*) where OH is lost from the parent ion. In contrast, *m*- and *p*-nitrotoluene (*7*) and trinitrobenzene (*8*) lose primarily NO, $NO_2$, and O from the parent ions. It is likely that the extensive hydrogen bonding between the methyl group and the *o*-nitro groups in TNT (*4*) is responsible for the initial loss of OH, rather than O. Virtually all of the *m/e* 211 peak is accounted for by the higher isotopes of the *m/e* 210 species, rather than by the loss of O from the parent ion (*m/e* 227). Finally, we failed to observe a metastable ion at *m/e* 196.1, which would confirm the loss of O from the parent ion.

The above result is contained in Figure 1, which outlines the major degradation reactions wherein the ring remains intact. The reactions in Figure 1 have been verified by the identification of metastables and the exact determination of mass numbers as indicated from the typical results given in Table II. In addition, the $^{15}N$ isotopic versions of TNT have enabled us to establish that species such as $C_7H_3N_3O_4$ (*m/e* 193) and $C_7H_4NO_2$ (*m/e* 134) exist in several forms. The results given in Figure 1 corroborate the majority of those presented in an earlier study (*6*) with the following minor exceptions. First, we were unable to detect the formation of $[C_7H_5N_3O_5]^{+\cdot}$ (*m/e* 211) from TNT via loss of oxygen, and, second, we failed to observe the presence of the fragment ions $[C_6H_2N_3O_5]^+$, $[C_7H_5N_3O_2]^{+\cdot}$, $[C_7H_5N_2O_4]^+$, and $[C_7H_5NO_2]^{+\cdot}$ in the high-resolution mass spectrum of TNT.

In Figure 1, the loss of three $NO_2$ groups from $(TNT)^+$ to form $[C_7H_5]^+$ is a reasonable sequence, as this is a common process in the case of nitro-containing aromatics and aliphatics (*9–11*). As with previous investigators (*6*), we have failed to detect the complete sequence, despite the fact that *m/e* 89 is the second most abundant ion in the TNT mass spectrum. During the course of our analysis, we observed a doubly charged ion, presumably $[C_7H_5N_2O_4]^{2+}$, at *m/e* 90.5. In addition, the metastable ion at 58.7 has been previously observed (*6*), which suggests the following sequence leading to $[C_7H_5]^+$, *m/e* 89:

$$[227]^{+\cdot} \xrightarrow{-NO_2^-} [181]^{2+} \xrightarrow{-NO_2^+} [135]^{+\cdot} \xrightarrow[m^*=58.7]{-NO_2\cdot} [89]^+ \quad (1)$$

The fact that $[C_7H_5]^+$ is the second most abundant ion in the TNT mass spectrum indicates that this species is unusually

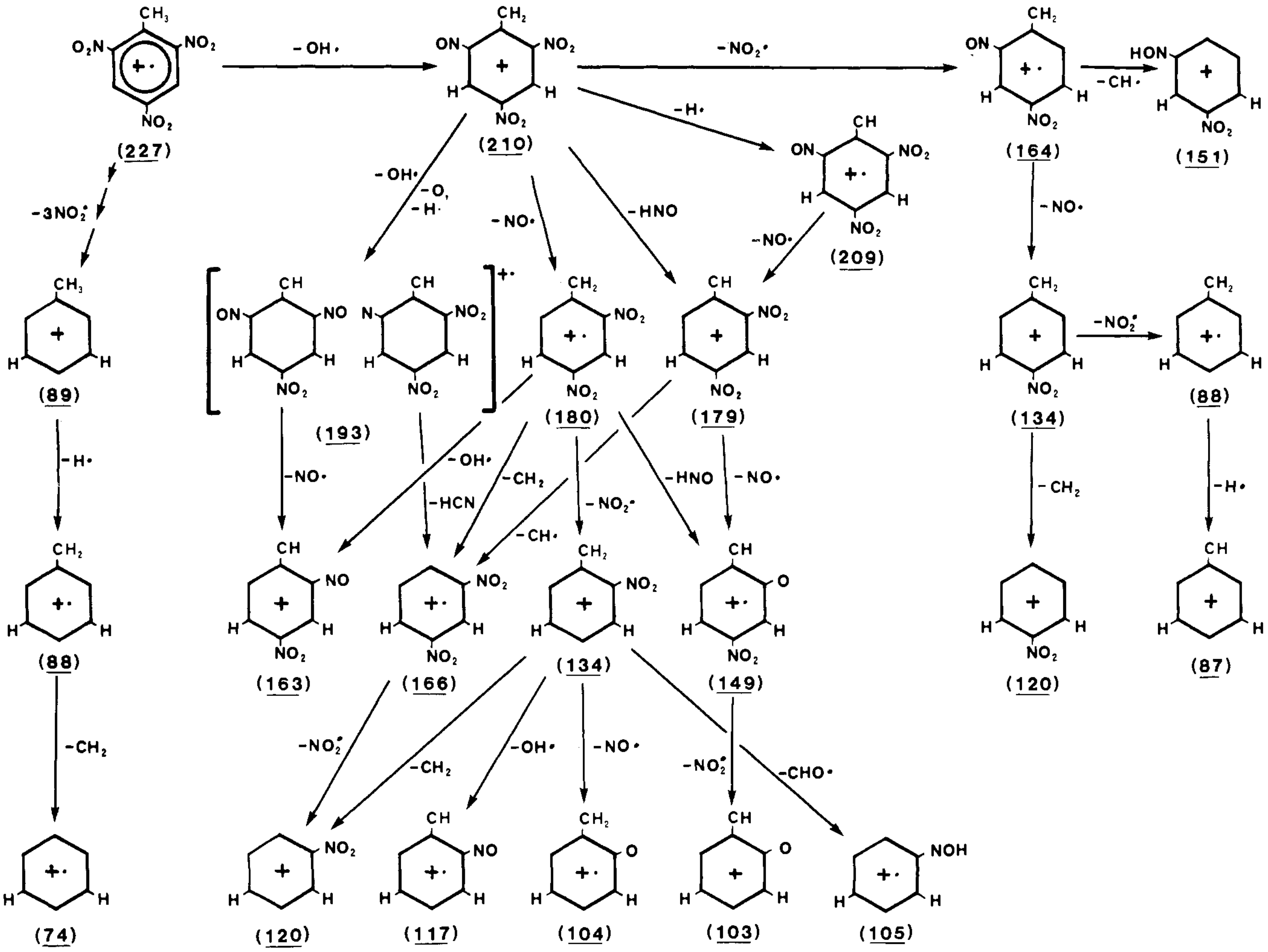

**Figure 1.** Fragmentation pathways for TNT in which the aromatic ring remains intact, deduced from high-resolution mass-spectral and metastable analysis.

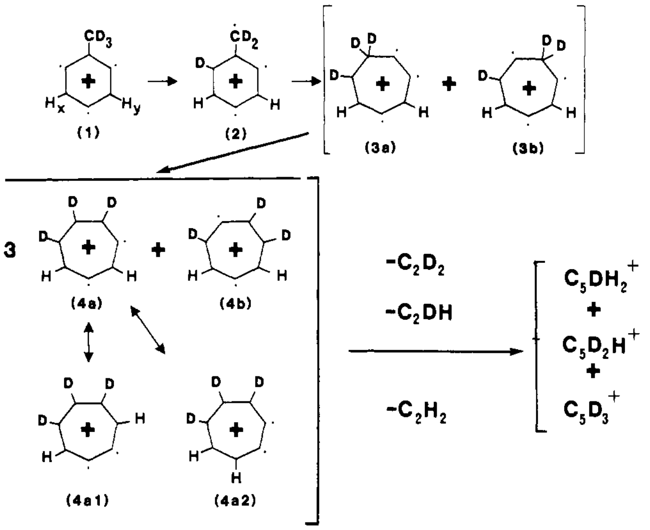

**Figure 2.** Rearrangement and fragmentation of the tropylium ion analogue of TNT.

stable, and has possibly undergone rearrangement. Examination of the data in Table I leads us to conclude that the $[C_7H_5]^+$ fragment ion is the same species previously detected (*12*) and is, in fact, a version of the tropylium ion as shown in Figure 2. The tropylium ion, $[C_7H_7]^+$, has been studied in detail by various investigators (*12–17*) using $^2H$ and $^{13}C$ labeling techniques. In the case of $[C_7H_7]^+$ derived from toluene and other similar compounds, the methyl and ring carbons and hydrogens are

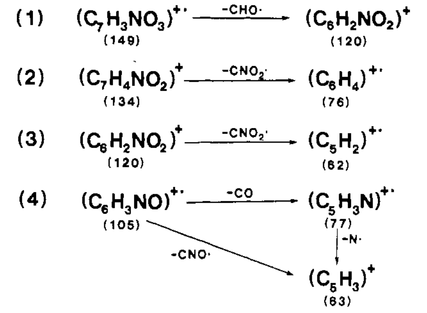

**Figure 3.** Fragmentation pathways for TNT in which the aromatic ring is cleaved, as verified by metastable analysis.

totally scrambled. In particular, there is a transfer of a methyl hydrogen to the ring, followed by a random ring insertion of $CH_2$. A hydrogen atom is then transferred from the ring $CH_2$ to a ring carbon, forming the highly symmetrical $[C_7H_7]^+$ tropylium ion. This species then undergoes loss of $C_2H_2$ to form $[C_5H_5]^+$.

In the case of TNT, loss of the $NO_2$ groups produces the species $[C_7H_5]^+$, which loses $C_2H_2$ in a manner similar to the tropylium ion, producing a metastable ion at *m/e* 44.6. In Figure 2 we have assumed that a methyl hydrogen (deuterium) is first transferred to the ring (structure **2**), followed by ring insertion of the $CH_2$ ($CD_2$) group to form structure **3a** or **3b**. A hydrogen (deuterium) from the ring $CH_2$ ($CD_2$) then migrates to form **4a** or **4b**. We will assume that only limited hydrogen (deuterium) migration occurs at this point, in which case **3a** converts only to **4a**, whereas **3b** converts to either **4a** or **4b**. If we assume that **4a** is the favored species, from both a

Table I. Relative Abundances in the High-Resolution Mass Spectra of TNT Isomers[a]

| *m/e* | TNT | α-d$_3$-TNT | (4-$^{15}$NO$_2$)-TNT | (2,6-$^{15}$NO$_2$)-TNT | (2,4,6-$^{15}$NO$_2$)-TNT | α-d$_3$-(2,4,6-$^{15}$NO$_2$)-TNT |
|---|---|---|---|---|---|---|
| 217 | | | | | | 1.9 |
| 216 | | | | | | 8.4 |
| 215 | | | | | 1.4 | 100 |
| 214 | | 1.8 | | 1.4 | 8.2 | 7.1 |
| 213 | | 9.2 | 1.4 | 10.5 | 100 | |
| 212 | 1.8 | 100 | 9.2 | 100 | 12.2 | |
| 211 | 9.3 | 6.3 | 100 | 4.8 | | |
| 210 | 100 | 2.7 | 3.5 | | | |
| 209 | 1.7 | | | | | |
| 198 | | | | | | 1.5 |
| 197 | | | | | 1.3 | 9.8 |
| 196 | | 1.6 | | 1.6 | 10.8 | |
| 195 | | 1.1 | 2.2 | 13.5 | | |
| 194 | 1.7 | 9.6 | 12.0 | | | |
| 193 | 7.8 | | | | | |
| 185 | | | | | | 1.2 |
| 184 | | 1.3 | | | | 13.8 |
| 182 | | 13.4 | 1.1 | | 17.8 | 3.2 |
| 181 | | 1.4 | 14.4 | 17.4 | | |
| 180 | 13.1 | 2.9 | 3.5 | 4.3 | | |
| 179 | 3.3 | | | | | |
| 168 | | | | | 4.1 | 5.7 |
| 167 | | | 1.3 | | 1.0 | |
| 166 | 3.5 | 4.0 | | 3.2 | 5.0 | 1.3 |
| | | 5.1 | | | | |
| 165 | 1.1 | | 2.7 | 3.2 | 1.9 | |
| 164 | 5.4 | 1.6 | 4.4 | 1.2 | | |
| 163 | 1.8 | | | | | |
| 156 | | | | | | 1.0 |
| 154 | | | | | | 1.0 |
| 152 | 1.3 | 1.6 | 1.2 | 1.0 | | |
| 151 | 1.9 | | | | | 5.6 |
| | | | | | | 13.2 |
| 150 | 1.1 | 4.9 | 8.8 | | 5.7 | |
| 149 | 7.7 | | | 7.8 | 1.3 | 2.5 |
| 140 | | | | | | 1.6 |
| 138 | | | | | | 4.0 |
| 137 | | 2.5 | | | | 9.2 |
| 136 | 1.1 | 6.6 | | | 1.2 | |
| 135 | 3.1 | 1.2 | 1.8 | 11.0 | 11.3 | 1.1 |
| 134 | 12.0 | 1.0 | 12.4 | 1.4 | 1.2 | |
| 133 | | | 3.0 | | | 2.5 |
| 121 | | | 1.8 | 1.6 | 2.8 | 3.0 |
| 120 | 2.1 | 2.1 | 1.7 | 1.3 | | |
| 119 | 1.2 | | | 1.7 | 1.1 | |
| 118 | 1.5 | 1.3 | | | 1.1 | |
| 117 | 1.8 | | 1.2 | | | |
| 116 | 1.5 | | | | | |
| 111 | | | | | | 3.9 |
| 109 | | | | | | 2.1 |
| 108 | | 1.2 | | | | 1.7 |
| | | 1.8 | | | | |
| 107 | | | | 2.2 | 2.0 | 1.5 |
| 106 | 2.3 | 1.5 | 2.7 | 1.4 | 1.5 | 2.5 |
| 105 | 2.0 | 1.1 | 3.8 | 1.5 | 1.5 | |
| | 1.8 | | 1.9 | | | |
| | | | 2.1 | | | |
| 104 | 2.8 | 1.3 | 3.2 | 2.9 | 2.9 | 1.7 |
| 103 | 2.6 | | 2.8 | 2.4 | 2.4 | 3.3 |
| 94 | 1.4 | 1.8 | 1.2 | | 1.0 | |
| 93 | | 2.5 | | 1.6 | 1.7 | 4.5 |
| 92 | 1.2 | 34.9 | 1.9 | | 1.0 | 38.9 |
| | 2.1 | 1.6 | | | | |
| | | 1.6 | | | | |
| 91 | 1.6 | 9.6 | 1.2 | 1.1 | 1.3 | 9.9 |
| | | | | 1.1 | | |
| 90 | 2.2 | 1.2 | 1.1 | 1.4 | 1.6 | 2.5 |
| | 1.9 | 1.8 | | 1.6 | 1.0 | 1.0 |
| | | 1.9 | | | | |
| 89 | 33.6 | 2.3 | 41.7 | 43.1 | 31.8 | 3.0 |
| | 3.1 | | | 1.1 | | |
| | | | | 27.7 | | |
| 88 | 7.4 | 1.7 | 8.7 | 6.5 | 7.4 | 2.1 |
| | 1.8 | | | | | |
| 87 | 4.9 | 1.6 | 6.5 | 4.4 | 4.9 | 1.7 |
| 86 | 3.3 | | 4.1 | 2.8 | 3.2 | |
| 85 | 1.6 | | 1.2 | | 1.3 | |
| 81 | | | | | 1.0 | 1.2 |
| | | | | | | 1.2 |
| 80 | 1.3 | 2.8 | | | | 3.5 |
| | | 1.8 | | | | |
| 79 | | 1.8 | | 1.2 | 1.4 | 2.8 |
| | | | | 2.0 | | 2.5 |
| | | | | | | 2.4 |
| 78 | 2.1 | 7.7 | 1.8 | 2.0 | 2.2 | 9.4 |
| | 1.0 | 2.1 | | 1.7 | | |
| 77 | 3.5 | 1.8 | 7.4 | 3.3 | 3.8 | 4.0 |
| | 2.6 | 1.1 | | 4.6 | 1.6 | |
| | | | | 1.5 | | |
| 76 | 10.8 | 2.4 | 14.1 | 9.5 | 11.0 | 3.6 |
| | 1.8 | 1.4 | 1.1 | 9.6 | | |
| 75 | 5.4 | 1.6 | 6.5 | 4.7 | 5.6 | 2.9 |
| | 1.0 | | | 7.4 | | |
| 74 | 5.6 | 2.5 | 6.4 | 4.8 | 5.5 | 3.2 |
| | | | | 7.3 | | |
| 73 | 1.3 | | | 2.0 | 2.0 | |
| | | | | 1.6 | | |
| 70 | | | | 2.4 | | 5.6 |
| 69 | 1.1 | 1.1 | 3.2 | 1.1 | 1.7 | 2.5 |
| 68 | | 1.1 | | | | 2.0 |
| | | 1.5 | | | | |
| 67 | 1.8 | 1.7 | 1.4 | 1.3 | 1.2 | 1.6 |
| 66 | 1.7 | 3.5 | 1.3 | 2.4 | 1.5 | 3.8 |
| | | 2.0 | | 1.5 | 1.4 | |
| | | 1.0 | | 1.2 | | |
| 65 | 2.4 | 8.8 | 2.1 | 2.2 | 2.0 | 13.3 |
| | 2.2 | 24.3 | | 1.7 | 3.8 | 2.2 |
| | | | | 2.6 | | |
| | | | | 2.1 | | |
| | | | | 1.5 | | |
| 64 | 2.2 | 11.3 | 5.0 | 3.5 | 2.6 | 15.8 |
| | | 32.4 | | 2.3 | | |
| | | 2.1 | | | | |
| 63 | 12.8 | 5.2 | 28.4 | 20.3 | 23.7 | 8.5 |
| | 32.8 | 14.7 | | 30.4 | | |
| 62 | 6.6 | 2.6 | 14.7 | 16.5 | 13.0 | 3.9 |
| | | 7.6 | | 11.0 | | |
| 61 | 3.2 | 2.4 | 2.6 | 3.7 | 2.6 | 1.3 |
| 60 | | | | 1.1 | 1.6 | |
| 57 | | | | | | 1.4 |
| | | | | | | 1.5 |
| 55 | 1.3 | | | 3.7 | 1.2 | 1.7 |
| 54 | | 2.8 | | | | 1.6 |
| | | 1.2 | | | | 1.4 |
| 53 | | 3.2 | | | | 5.4 |
| | | 9.1 | | | | |
| 52 | 1.2 | 3.0 | 1.5 | 1.2 | 1.0 | 4.6 |
| | | 8.6 | | | 2.8 | |
| 51 | 4.0 | 2.3 | 9.9 | | 14.1 | |
| 50 | 3.5 | 1.1 | 7.5 | | 11.2 | |

[a] Only abundances greater than 1% are included in the *m/e* range 50–233.

statistical and energetic point of view, we can arrive at a satisfactory solution. This is accomplished by considering $C_2H_2$ elimination from **4a** and its alternate structures, **4a1** and **4a2** (Figure 2). **4a1** and **4a2**, which are analogous to benzyne, are formed from **4a** by the migration of a single ring hydrogen ($H_y$, structure **1**). Loss of $C_2H_2$ from these three isomers of $[C_7H_2D_3]^+$ will statistically result in the formation of $[C_5H_2D]^+$, $[C_5HD_2]^+$, and $[C_5D_3]^+$ in the abundance ratio of 6:4:1, respectively. Experimentally, we observe these three ions in the ratio 11.3:8.8:2.0 from α-d$_3$-TNT and 15.8:13.3:3.8 for α-d$_3$-

J. Chem. Eng. Data 1984, 29, 97-99

Table II. Exact Masses of Selected Ions in the Mass Spectrum of TNT

| observed mass, amu | emperical formula | calcd mass, amu | deviation, mmu |
|---|---|---|---|
| 210.0149 | $C_7H_4N_3O_5$ | 210.0151 | −0.2 |
| 209.0076 | $C_7H_3N_3O_5$ | 209.0073 | +0.3 |
| 193.0121 | $C_7H_3N_3O_4$ | 193.0124 | −0.3 |
| 180.0171 | $C_7H_4N_2O_4$ | 180.0171 | 0 |
| 179.0088 | $C_7H_3N_2O_4$ | 179.0092 | −0.4 |
| 166.0017 | $C_6H_2N_2O_4$ | 166.0015 | +0.2 |
| 164.0222 | $C_7H_4N_2O_3$ | 164.0222 | 0 |
| 163.0144 | $C_7H_3N_2O_3$ | 163.0144 | 0 |
| 151.0148 | $C_6H_3N_2O_3$ | 151.0143 | +0.5 |
| 149.0113 | $C_7H_3NO_3$ | 149.0113 | 0 |
| 134.0241 | $C_7H_4NO_2$ | 134.0242 | −0.1 |
| 120.0088 | $C_6H_2NO_2$ | 120.0086 | +0.2 |
| 117.0215 | $C_7H_3NO$ | 117.0215 | 0 |
| 105.0218 | $C_6H_3NO$ | 105.0215 | +0.3 |
| 104.0262 | $C_7H_4O$ | 104.0263 | −0.1 |
| 103.0185 | $C_7H_3O$ | 103.0184 | +0.1 |
| 89.0392 | $C_7H_5$ | 89.0392 | 0 |
| 88.0313 | $C_7H_4$ | 88.0313 | 0 |
| 87.0236 | $C_7H_3$ | 87.0235 | +0.1 |
| 77.0265 | $C_5H_3N$ | 77.0266 | −0.1 |
| 76.0316 | $C_6H_4$ | 76.0313 | +0.3 |
| 74.0161 | $C_6H_2$ | 74.0156 | +0.5 |
| 63.0246 | $C_5H_3$ | 63.0235 | +1.1 |
| 62.0169 | $C_5H_2$ | 62.0156 | +1.3 |

(2,4,6-$^{15}NO_2$)-TNT, as shown in Table I. Other mechanisms, including the total scrambling of hydrogen and deuterium, produce generally lower ratios of $[C_5H_2D]^+$ to $[C_5HD_2]^+$ and $[C_5H_2D]^+$ to $[C_5D_3]^+$ than is found experimentally. It is likely that other scrambling does occur in the $[C_7H_2D_3]^+$ ion in addition to that which we have considered. However, the exact solution undoubtedly includes a major contribution from the proposed pathway.

Finally, there is the question of ring fragmentation in TNT. We have verified by metastable analysis a limited number of ring degradation reactions where a ring carbon atom is involved. These are summarized in Figure 3.

**Registry No.** TNT, 118-96-7; α-$d_3$-TNT, 52886-05-2; (4-$^{15}NO_2$)-TNT, 83858-97-3; (2,6-$^{15}NO_2$)-TNT, 86456-41-9; (2,4,6-$^{15}NO_2$)-TNT, 86456-42-0; α-$d_3$-(2,4,6-$^{15}NO_2$)-TNT, 86456-43-1; 2,4-dinitrotoluene, 121-14-2; 4-nitrotoluene, 99-99-0; toluene, 108-88-3.

## Literature Cited

(1) Shackelford, S. A.; Beckmann, J. W.; Wilkes, J. S. *J. Org. Chem.* **1977**, *42*, 4201.
(2) Beckmann, J. W.; Wilkes, J. S.; McGuire, R. R. *Thermochim. Acta* **1977**, *19*, 11.
(3) Guidry, R. M.; Davis, L. P. *Thermochim. Acta* **1979**, *32*, 1.
(4) Carper, W. R.; Davis, L. P.; Extine, M. W. *J. Phys. Chem.* **1982**, *86*, 459.
(5) Dennis, W. H.; Rosenblatt, D. H.; Blucher, W. G.; Coon, C. L. *J. Chem. Eng. Data* **1975**, *20*, 202.
(6) Bulusu, S.; Axenrod, T. *Org. Mass Spectrom.* **1979**, *14*, 585.
(7) Myerson, S.; Puskas, I.; Fields, E. K. *J. Am. Chem. Soc.* **1966**, *88*, 4974.
(8) Myerson, S.; VanderHaar, R. W.; Fields, E. K. *J. Org. Chem.* **1972**, *37*, 4114.
(9) Budzikiewicz, H.; Djerassi, C.; Williams, D. H. "Mass Spectrometry of Organic Compounds"; Holden-Day: San Francisco, CA, 1967.
(10) Collin, J. *Bull. Soc. R. Sci. Liege* **1954**, *23*, 194.
(11) Larkins, J. T.; Saalfield, F. E.; Kaplan, L. *Org. Mass Spectrom.* **1969**, *2*, 213.
(12) Rinehart, K. L.; Buchholz, A. C.; Van Lear, G. E.; Cantrill, H. L. *J. Am. Chem. Soc.* **1968**, *90*, 2983.
(13) Rylander, P. N.; Myerson, S.; Grubb, H. M. *J. Am. Chem. Soc.* **1957**, *79*, 842.
(14) Myerson, S. *J. Am. Chem. Soc.* **1963**, *85*, 3340.
(15) Meyer, F.; Harrison, A. G. *J. Am. Chem. Soc.* **1964**, *86*, 4757.
(16) Siegel, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5277.
(17) Howe, I.; McLafferty, F. W. *J. Am. Chem. Soc.* **1971**, *93*, 99.

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# Preparation of 2-Amino-2,3-dihydrobenzimidazole and Its Derivatives

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**New compounds, derivatives of 2-amino-2,3-dihydrobenzimidazole, were prepared by modified Gabryel reaction of 2-chloro-2,3-dihydrobenzimidazole with potassium phthalimide. Their mass spectra are presented.**

The well-known methods of synthesis of 2,3-dihydrobenzimidazole derivatives are the reactions of aldehydes or ketones with *o*-phenylenediamine. The products of the reactions are often a mixture of compounds that are difficult to separate (*1*–*3*). Recent publications describe the synthesis of derivatives of 2-thioxo-2,3-dihydrobenzimidazole in the reaction of *o*-phenylene diisocyanate with amines (*4*), and of derivatives of 2-oxo-2,3-dihydrobenzimidazole which were obtained in the Curtius rearrangement (*5*).

2-Amino-2,3-dihydrobenzimidazole and its derivatives are new compounds.

In ref *6* was described a method of preparation of 2-chloro-2,3-dihydrobenzimidazole from chloroform and *o*-phenylenediamine.

Table I. Melting Points, NMR Data, and Yields of 2-Amino-2,3-dihydrobenzimidazole and Its Derivatives

| compd | mp, °C | $^1H$ NMR δ | yield, % |
|---|---|---|---|
| 1 | 210 | 7 (d, $J = 11$ Hz, 1 H, 2-H, CH), 6.6 (NH), 6.8–7.4 (ArH) | 94 |
| 5′ | 102 | 6.5 (d, $J = 5$ Hz, 1 H, 2-H, CH), 4.4 (NH), 6.2–6.8 (ArH) | 23 |
| 2 | 166 | | 90 |
| 3 | sub 340 | | 59 |
| 4 | sub 320, romb cryst | | 95 |
| 5 | 136 | | 11 |
| 5‴ | 98 | | 98 |
| 6 | 211 | | 8.7 |

The methods of preparation of 2-amino-2,3-dihydrobenzimidazole and its derivatives are presented in Scheme I. Melting points, NMR data, and yields of these compounds are presented in Table I.

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