α and β are constants and t is the temperature in °C. Each composition was measured at four temperatures, except the 35.0 mole % $AlCl_3$ which was measured at six temperatures. The standard deviations for the least squares fit and the experimental temperature ranges are listed in Table I. Molar volumes were calculated at 220° C. for direct comparison with previous volume measurements on the $AlCl_3$-NaCl system (Table I).

A pycnometric method was used by Keneshea and Cubicciotti (*5*) to measure the density of pure $BiCl_3$. Their results are listed in Table I and agree quite well with the results reported here. More recently, Johnson and Cubicciotti (*4*) used the float method to obtain $BiCl_3$ liquid densities at higher temperatures ranging up to the critical temperature. These authors compared their high temperature results with the low temperature pycnometric results (*5*) and found them to be in good agreement.

Molar volumes for the $AlCl_3$-NaCl system showed a maximum negative deviation from linearity of the order of 20%. This was attributed at least in part to the strong acidic nature of $AlCl_3$ resulting in the formation of $AlCl_4^-$ and $Al_2Cl_7^-$. The $AlCl_3$-$BiCl_3$ system showed a maximum negative deviation of the order of 13% at comparable compositions and temperatures. Although this may seem surprising considering the acidic nature of $BiCl_3$, it probably is just another indication of the extreme acidity of $AlCl_3$ relative to most other solvents.

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Heats of Combustion of *trans*-Stilbene and *trans*-2,2′,4,4′,6,6′-Hexanitrostilbene (HNS)

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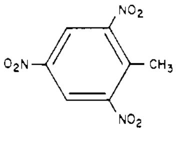
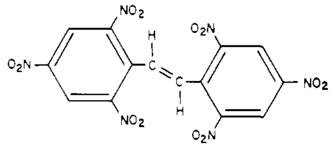
The standard heats of combustion, $\Delta H^\circ_{c\,298}$, of *trans*-stilbene (c) and *trans*-2,2′,4,4′,6,6′-hexanitrostilbene(c) were measured in an oxygen bomb calorimeter and were −1759.28 and −1535.54 kcal. mole^{-1}, respectively. Estimated uncertainties of these results, respectively, were 0.93 and 1.08 kcal. moles^{-1} including contribution of errors from both random and systematic sources. With these results, the standard heats of formation, $\Delta H^\circ_{f\,298}$, of *trans*-stilbene(c) and *trans*-2,2′,4,4′,6,6′-hexanitrostilbene(c) were −32.68 and −13.89 kcal. mole^{-1}, respectively. The standard heats of formation of the gas phases were −12.0 and +29.2 kcal. mole^{-1}, respectively. In the light of these results, and analogous data for toluene(g) and trinitrotoluene(g), the addition of six nitro groups to *trans*-stilbene may be interpreted as weakening the central C=C bond by 34.1 kcal. mole^{-1}.

RECENTLY, Shipp successfully synthesized *trans*-2,2′,-4,4′,6,6′-hexanitrostilbene, henceforth designated as HNS (*13, 14*). The close relationship of HNS to 2,4,6-trinitrotoluene (TNT) immediately becomes obvious by a comparison of their structural formulas:



TNT



HNS

HNS is a solid explosive somewhat less sensitive than TNT. Because of its low vapor pressure and good heat stability, it is suitable for applications requiring storage in a high vacuum and subjection to temperature extremes, such as may be encountered in the exploration of the moon's surface. To obtain information about the energy of HNS, as is required to use it effectively as an explosive, the authors have determined the heat of formation with respect to the elements. This objective of the present work was accomplished by measuring the heat of combustion of HNS.

It also was convenient to consider as a subsidiary objective the effect of adding six nitro groups to the aromatic nuclei of *trans*-stilbene on the C=C bond linking them. This effect may be estimated by combining combustion

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measurements on *trans*-stilbene and HNS with some other auxiliary data, and is shown in the last section of the text.

MATERIALS

***trans*-Stilbene.** The sample was zone-refined *trans*-stilbene from a commercial supplier. The compound was in the form of various-sized chunks of translucent crystal. The supplier reported a purity of about 99.99%. No check of the purity was made in this laboratory.

***trans*-2,2′,4,4′,6,6′-Hexanitrostilbene.** The sample consisted of 25 grams of HNS synthesized by Shipp at the Naval Ordnance Laboratory (NOL). The physical appearance of the compound was fine crystalline needles, delicate yellow in color. The impurities were estimated at NOL to total less than 0.03% by gas-liquid chromatography. An infrared spectrum made at NOL indicated the compound is the trans isomer.

The following tests made in this laboratory showed that the hygroscopicity or volatility of HNS is not sufficient to be of any significance to the measurements. There was no increase in the weighg of a 0.6-gram sample of HNS in an open platinum crucible for 5 days and no weight loss of the sample kept in a $Mg(ClO_4)_2$ desiccator for 5 hours.

REACTIONS STUDIED

The energy releases accompanying the reactions in Equations 1 and 2

$$C_{14}H_{12}(c) + 17O_2(g) \rightarrow 14CO_2(g) + 6H_2O(l) \quad (1)$$

$$C_{14}H_6N_6O_{12}(c) + 19/2\ O_2(g) \rightarrow 14CO_2(g) + 3H_2O(l) + 3N_2(g) \quad (2)$$

were measured in an oxygen bomb calorimeter. The initial oxygen pressure in all runs was approximately 30 atm.

EXPERIMENTAL PROCEDURES

Apparatus. The NBS rotating bomb calorimeter, designated RBC-1, was used in the heat measurements. The bomb volume is 340 cc. Similar calorimeters have been described adequately elsewhere (*17*). The calorimetric procedures, too, have been described previously (*9*). (The bomb was not rotated in any of the experiments described in this article because the energy of solution of the oxides of nitrogen was anticipated to be small.)

Preparation of Samples. For each *trans*-stilbene run, two to four chunks of the zone-refined crystals were selected from the sample bottle to a total of approximately 0.5-gram. No further preparation was necessary. The chunks burned cleanly and easily.

Two pellet press setups were used in the preparation of HNS samples suitable for combustion. (Burning loose HNS powder resulted in incomplete and unsatisfactory combustion.)

In the first setup, at the Naval Ordnance Laboratory, three 1-gram pellets were prepared with a vertical lever press by applying a compression of about 20,000 p.s.i. Two of these pellets were used in preliminary experiments; the third was used as the sample for the first run in the reported measurements.

In the second setup, in this laboratory, seven pellets, each weighing about 1.4 grams, were prepared in a torsional lever press by applying a compression probably in excess of 30,000 p.s.i. All seven pellets were used in the final measurements.

Danger. *HNS must be considered a hazardous compound and should be handled cautiously.* In both pellet press arrangements, the operator was protected from possible accidents by a metal housing enclosing the press.

Ignition Arrangement. The authors preferred in combustion experiments to ignite the sample at a surface not in contact with the platinum crucible. Because the bomb is assembled in an upright position but is fired in an inverted one (to protect gaskets at the several ports), an occasional ignition failure would result when the cotton thread fuse moved away from contact with the sample. To prevent this occurrence in these experiments on HNS, stilbene, and benzoic acid, the fuse was passed twice over the sample and through three holes in the crucible in a novel arrangement shown in Figure 1. No ignition failures were due to the fuse not igniting a sample.

Determination of Stoichiometry. In all runs with HNS a small amount of carbon, varying from 0.2 to 1.3 mg., was formed as a combustion product. The carbon was observed as a fine suspension of black particles in the bomb washings. The carbon was filtered from the washings and quantitatively determined as CO_2 in a combustion train.

In addition, the CO_2 in the gaseous combustion products was quantitatively collected by flowing the product gases from the bomb through a weighed absorber filled with Ascarite and magnesium perchlorate. CO was tested for, but not observed. Thus the amount of carbon produced, was estimated from the difference of the carbon dioxide calculated (equivalent to the mass of sample taken) and the carbon dioxide actually collected.

The agreement between the two methods of estimating the carbon formed was good in most of the experiments. The results given by the two methods are summarized in Table I. Analysis of the bomb gases was probably the more accurate method. This conclusion, based on appraisal of the two methods, was strengthened by the fact that the standard deviation of the mean of $\Delta H_c^\circ/M[\text{HNS(c)}]$ was a little smaller when the carbon corrections were based on analyses of the bomb gases than when based on the analyses of residues.

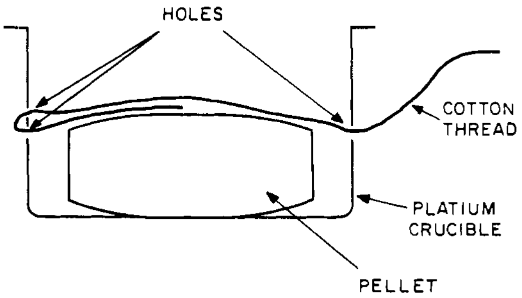

Figure 1. Ignition arrangement of fuse and sample

Table I. Summary of Carbon Production in HNS Runs

Run No.	Mass of Carbon, Mg. From analysis of bomb gases	Mass of Carbon, Mg. From analysis of residue
1	0.404	0.4
2	0.545	0.6
3	0.548	0.9
4	0.502	0.8
5	1.294	1.1
6	0.527	0.3
7	0.734	0.4
8	0.171	0.9

As time was limited, it was not possible to perform CO_2 analyses on the products of combustion of *trans*-stilbene. Because the *trans*-stilbene burned cleanly, a stoichiometric conversion to CO_2 was assumed.

During the combustion of HNS, a significant amount of nitrogen in the compound is fixed to HNO_3. To facilitate the solution of the acid in the bomb liquid, the 1 ml. of water, which is added to the bomb routinely, was introduced from a pipet while the bomb was rotated beneath it to maximize the surface area of the water over the bomb wall. The amount of HNO_3, formed was determined by titration with standard NaOH solution after the CO_2 was collected. In a typical HNS experiment, about 0.6 meq. of HNO_3 was produced.

Calibration of the Calorimeter. The calorimeter was calibrated in five runs with benzoic acid, NBS standard sample 39*i*. The mass of the benzoic acid used was selected to give approximately the same temperature rise of the calorimeter (from 30.5° to 31.9° C.) as in the stilbene and HNS measurements. The energy equivalent, ϵ, was established to be 15,256.9 J. °K.$^{-1}$ with a standard deviation of the mean of 1.6 J. °K.$^{-1}$.

CALCULATIONS

Auxiliary Quantities. The following constants were used in the calculations.

	ρ, Grams/Cc.	C_p, Cal./Deg. Gram
HNS	1.740 (*13*)	0.40 (estimated)
trans-Stilbene	0.970 (*8*)	0.309 (*16*)

Molecular weights were calculated from the 1961 Table of Relative Atomic Weights (*2*). The calorie is 4.184 joules. The gas constant R has the value 8.3143 J. °K.$^{-1}$ mole^{-1}.

Computer Program. The results of the calibration, HNS, and *trans*-stilbene, experiments were calculated on an electronic computer at the NBS. The program (*15*) was written by Shomate. The correction for the formation of the small amount of carbon was inserted into the program by considering the carbon as an auxiliary material, for which the heat of combustion was taken with inverse sign. The electrical energy needed for ignition was assumed to be the same for calibration and measurement experiments and had previously been observed to be very small, so no correction for this was applied.

Results of Calculations. Table II shows the results of a typical *trans*-stilbene experiment and a typical HNS experiment. The format and abbreviations follow the presentation given by Good and Scott (*7*).

EXPERIMENTAL RESULTS

Table III summarizes the values of ΔH_c° [*trans*-stilbene(c)] for the four experiments performed and ΔH_c° [HNS(c)] for the eight experiments performed, respectively, each series being numbered in chronological order of measurement.

The observed standard deviation from these tables amounts in each case to 0.013% and that for the calibration of the calorimeter to 0.016%. Hence, the over-all imprecision for the experimental determination expressed in 2-sigma limits is $\pm\ 2[(0.013)^2 + (0.016)^2]^{1/2} = \pm 0.043\%$. Adding ±0.01% to reflect the uncertainty in the energy of combustion of benzoic acid, the total uncertainty in the standard heat of combustion of *trans*-stilbene(c) is 0.053% or 0.93 kcal. mole^{-1}. For the standard energy of combustion of HNS, an additional component of ±0.017% needs to be included for the possible error in the correction for incomplete combustion of HNS, which the authors estimate at 20%. This makes the total uncertainty 0.070%, or 1.08 kcal. mole^{-1} in the heat of combustion of HNS. See Eisenhart (*5*) for a discussion of the combination of random and systematic errors which has been followed here.

Table II. Typical Experiments of Combustion of HNS and *trans*-Stilbene

	trans-Stilbene Run No. 1	HNS Run No. 2
m' (sample), grams	0.534703	1.454368
m'' (carbon), grams	0.00	0.000545
Δt_c, ° C.	1.42961	1.36680
ϵ(calor)$(-\Delta t_c)$, joules	−21,811.36	−20,853.14
ϵ(cont)$(-\Delta t_c)$, joules	−21.92	−23.35
$-\Delta E$, dec (HNO_3), joules	0.21	42.47
ΔE, corr. to st. states, joules	5.81	32.02
$m''\ \Delta E_c^\circ/M$ (carbon), joules	0.00	−17.87
$-m'''\ \Delta E_c^\circ/M$ (fuse), joules	18.24	18.66
$m'\ \Delta E_c^\circ/M$ (sample), joules	−21,809.02	−20,801.21
$\Delta E_c^\circ/M$ (sample), joules gram^{-1}	−40,787.16	−14,302.58
$\Delta E_c^\circ/M$ (sample), kcal. mole^{-1}	−1757.16	−1539.09
ΔnRT (sample), kcal. mole^{-1}	−1.78	4.44
$\Delta H_c^\circ/M$ (sample), kcal. mole^{-1}	−1758.94	−1534.65

Table III. Summary of Combustion Runs

Run No.	$-\Delta H_c^\circ$, Kcal. Mole^{-1} at 298.15 ° K.
Trans-Stilbene	
1	1758.94
2	59.07
3	59.17
4	59.94
Mean	1759.28
Std. dev. of the mean	0.225
HNS	
1	1535.92
2	34.65
3	35.15
4	35.31
5	36.31
6	36.11
7	35.76
8	35.08
Mean	1535.54
Std. dev. of the mean	0.203

Coops and Hoÿtink measured the heat of combustion of *trans*-stilbene to be −1759.35 ±0.12 kcal. mole^{-1} (*3*); Richardson and Parks had previously found a heat of combustion of −1757.0 ±0.67 kcal. mole^{-1} (*10*). The value reported in the present work is in excellent agreement with the value of Coops and Hoÿtink. There is no other measurement of the heat of combustion of HNS in the literature.

HEATS OF FORMATION OF *TRANS*-STILBENE AND HNS

Referring back to Equations 1 and 2 and taking $\Delta H_f^\circ[CO_2(g)]$ and $\Delta H_f^\circ[H_2O(l)]$ equal to −94.051 kcal. mole^{-1} (*18*) and −68.315 kcal. mole^{-1} (*18*), respectively, ΔH_f°[*trans*-stilbene(c)] is calculated to be −32.76 kcal. mole^{-1} and ΔH_f°[HNS(c)], −13.88 kcal. mole^{-1}.

When ΔH_s is taken, respectively, for *trans*-stilbene and HNS, to be 20.68 kcal. mole^{-1} (*6*) and 43.1 kcal. mole^{-1} (*11*), and combined with the above heats of formation, then ΔH_f°[*trans*-stilbene(g)] is equal to −12.0 kcal. mole^{-1} and ΔH_f°[HNS(g)] is equal to +29.2 kcal. mole^{-1} at 298.15 °K.

BOND ENERGY, $E(C=C)$, DIFFERENCE IN *TRANS*-STILBENE AND HNS

Effect of Adding Six Nitro Groups to *trans*-Stilbene on the $E(C=C)$. With $\Delta H_f^\circ[\text{HNS(g)}]$ and $\Delta H_f^\circ[\textit{trans}\text{-stilbene(g)}]$ now available, it is possible to make an estimate of $E(C=C)$ in HNS relative to $E(C=C)$ in *trans*-stilbene. In the discussion that follows, bond energy constancy is assumed with the exception of $E(C=C)$.

Consider the hypothetical reactions of Equation 3 involving HNS and trinitrotoluene (TNT) and Equation 4 involving stilbene (S) and toluene (T), respectively.

$$\underset{[\text{HNS}](g)}{C_6H_2(NO_2)_3CH=CHC_6H_2(NO_2)_3(g)} + 2H_2(g) = \underset{[\text{TNT}](g)}{2CH_3C_6H_2(NO_2)_3(g)} \quad (3)$$

$$\underset{[\text{S}](g)}{C_6H_5CH=CHC_6H_5(g)} + 2H_2(g) = \underset{[\text{T}](g)}{2C_6H_5CH_3(g)} \quad (4)$$

For Equation 3

$$\Delta H_r^\circ = 2\Delta H_f^\circ[\text{TNT(g)}] - \Delta H_f^\circ[\text{HNS(g)}] \quad (5)$$

and for Equation 4

$$\Delta H_r^\circ = 2\Delta H_f^\circ[\text{T(g)}] - \Delta H_f^\circ[\text{S(g)}] \quad (6)$$

ΔH_r° in Equations 5 and 6 is also equal in each case to the sum of the energy of making four C—H bonds, $-4E(\text{C—H})$, and the energies of breaking one $C=C$ bond, $E(C=C)$, and two H—H bonds, $2E(\text{H—H})$. Thus, for Equation 5

$$E(C=C)_{\text{HNS}} = 2\Delta H_f^\circ[\text{TNT(g)}] - \Delta H_f^\circ[\text{HNS(g)}] + 4E(\text{C—H}) - 2E(\text{H—H}) \quad (7)$$

and for Equation 6

$$E(C=C)_{\text{S}} = 2\Delta H_f^\circ[\text{T(g)}] - \Delta H_f^\circ[\text{S(g)}] + 4E(\text{C—H}) - 2E(\text{H—H}) \quad (8)$$

Equations 7 and 8 have probably less validity than does their difference, which may be reasonably interpreted as a change in the $E(C=C)$ bond. Subtracting Equation 8 from Equation 7 and letting $E(C=C)_{\text{HNS}} - E(C=C)_{\text{S}} = \Delta E(C=C)$,

$$\Delta E(C=C) = 2\Delta H_f^\circ[\text{TNT(g)}] - \Delta H_f[\text{HNS(g)}] - 2\Delta H_f^\circ[\text{T(g)}] + \Delta H_f^\circ[\text{S(g)}] \quad (9)$$

Using the previously determined heats of formation for HNS(g) and *trans*-stilbene(g) and accepting $\Delta H_f^\circ[\text{T(g)}] = 11.96$ kcal. mole^{-1} (*12*) and $\Delta H_f^\circ[\text{TNT(g)}] = 15.5$ kcal. mole^{-1} (*1,4*), by substituting them into Equation 9, $\Delta E(C=C) = -34.1$ kcal. mole^{-1}. That is, the addition of six nitro groups to *trans*-stilbene weakens the $C=C$ bond by 34.1 kcal. mole^{-1}. Of course, this method of calculation does not demonstrate that the bond weakening is localized in the $C=C$ bond; some other type of evidence would be necessary to demonstrate that.

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NOMENCLATURE

$E(C=C)$ = energy of breaking an ethylenic linkage
m' = mass of sample
m'' = mass of carbon
m''' = mass of combustible fuse
ΔE, corr. to st. states = change of internal energy from actual to thermodynamic standard state
ΔE, dec(HNO_3) = energy of decomposition of nitric acid to the elements
Δt_c = corrected temperature rise
ϵ(calor) = energy equivalent of the standard calorimeter
ϵ(cont) = energy equivalent of the initial bomb contents

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