mass. Substituting, one obtains

$$k_c = [k/8\pi^3 I]^{1/2} T^{1/2} e^{-E_c/RT} \qquad \text{(B3)}$$

In Arrhenius form (T = 300°K) this becomes

$$k_c = [k/8\pi^3 I]^{1/2} 10^{1.5} 10^{-(E_c + 0.3)/\theta} \qquad \text{(B4)}$$

where $[k/8\pi^3 I]^{1/2} 10^{1.5} = A_c$. E_c should be similar to the rotation barrier[5b,13,14] of the analogous nitroso radical **1**. Therefore, $E_c \approx 4 \pm 0.5$ kcal mol^{-1} and, after appropriate substitution in (B3), one obtains $k_c = 10^{11.4} 10^{-4.3/\theta}$ sec^{-1}.

Enthalpies of Formation for Globular Molecules. III. Succinonitrile and Triethylenediamine[1]

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Abstract: Enthalpies of combustion have been measured for crystalline succinonitrile and 1,4-diazabicyclo[2.2.2]-octane, and the derived enthalpies of formation at 298.15°K in the crystalline state, $\Delta H_f°$(c), are 33.38 ± 0.16 and 6.75 ± 0.96 kcal/mol, respectively. Adjuvant data for both compounds permit evaluation at 298.15°K of the corresponding enthalpy values, $\Delta H_f°$(g), for the gaseous compounds as 50.11 ± 0.16 and 21.6 ± 1.6 kcal/mol. The strain energies of the compounds are discussed.

Two interesting, nitrogen-containing plastically crystalline substances, which already have been studied by thermophysical methods over an extended range of temperature, are here examined by thermochemical means. Although data for succinonitrile[3] and for 1,4-diazabicyclo[2.2.2]octane[4] (triethylenediamine) do exist in the literature, that on the former did not appear to be a definitive value and that on the latter led to an interpretation of strain energies clearly at variance with those observed for homologous bicyclo compounds.[5]

Experimental Section

Preparation, purification, and characterization details of the calorimetric samples as 99.93% pure succinonitrile[6,7] and 99.7% pure triethylenediamine,[8,9] the constructional features and operational procedures of the rotating-bomb calorimeter, and reduction of data[10] have been described elsewhere. The standard symbolism has been retained here.[11] Calibration of the calorimeter with NBS standard benzoic acid sample 39i[12] for these compounds yielded $\mathcal{E}^0$(calor) = 3969.63 ± 0.10 cal °K^{-1} for the determinations on succinonitrile, 3973.44 ± 0.06 cal °K^{-1} for those on the diamine. To protect both substances from CO_2 and H_2O (triethylenediamine is especially sensitive and fairly volatile also), the pellets were loaded into Type A DuPont Mylar (polyester) bags. The $\Delta E_c°/M$ for this sample of Mylar was determined in a separate series of experiments to be −5479.30 + (0.2524*RH*) cal/g. Here, *RH* is the relative humidity expressed in per cent. The ΔE_c of the cotton fuse was −4108 cal g^{-1}. A deep, platinum crucible was used for combustions of both substances; a platinum baffle was found advantageous to avoid soot during combustion of the diamine.

All values are given in defined thermochemical calories equal to 4.1840 J; 1961 atomic weights are used and the ice point is taken as 273.15°K. The values of the parameters used for converting the measured quantities to weights *in vacuo*, to the isothermal process, and to standard states are given in Table I. These values were obtained from the literature. Those in parentheses were estimated by analogy with those of similar materials. Contributory enthalpies of formation, $\Delta H_f°$, were taken from ref 13. They are −94.051 kcal mol^{-1} for carbon dioxide (g) and −68.315 kcal mol^{-1} for water (l).

Table I.

Substance	Density, g cm^{-3}	C_p, cal (g °K)$^{-1}$	$(\partial V/\partial T)_p$, l. g^{-1} °K^{-1}
Succinonitrile	1.04	0.4345	(0.52 × 10^{-6})
Triethylenediamine	1.147	0.3255	(0.52 × 10^{-6})
Mylar	1.38	0.315	(0.111 × 10^{-6})

Results

Calorimetric Results. Seven combustions were made of succinonitrile and six of triethylenediamine. Data from combustions selected as typical for each compound are summarized in Table II. The results of the individual combustion experiments in terms of $-\Delta E_c°/M$ at 298.15°K are summarized in Table III and refer to the following reaction

$$C_4H_4N_2(c) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l) + N_2(g)$$

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[1] This research was supported in part by the U. S. Atomic Energy Commission.

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Table II. Summary of Typical Combustion Experiments[a]

Compound	Succinonitrile	Triethylenediamine
m'(compound), g *in vacuo*	0.890402	0.694559
$\Delta t = t_f - t_i - \Delta t_{corr}$, °K	1.65937	1.65983
$\mathcal{E}$(calor) $(-\Delta t)$, cal	−6527.27	−6509.40
$\mathcal{E}$(cont) $(-\Delta t)$,[b] cal	−7.53	−8.10
ΔE_{ign}, cal	0.29	0.30
$\Delta E^f_{dec}(HNO_3 + HNO_2)$, cal	18.25	15.23
ΔE, corr to std states, cal	3.63	1.90
$-m''\Delta E_c°/M$(Mylar), cal	431.72	427.88
$-m'''\Delta E_c°/M$(fuse), cal	6.47	6.49
$-m'\Delta E_c°/M$(compound), cal	6073.89	6065.13
$-\Delta E_c°/M$(compound), cal g^{-1}	6821.53	8732.36

[a] The symbols are standard[11] except as noted. [b] $\mathcal{E}^i(\text{cont})(t_i - t_h) + \mathcal{E}^f(\text{cont})(t_h - t_f + \Delta t_{corr})$.

Table III. Summary of Combustion Results at 298.15°K

Compound	Succinonitrile	Triethylene-diamine
$-\Delta E_c°/M$, cal g^{-1}	6820.18	8727.51
	6820.39	8732.17
	6819.18	8732.51
	6817.93	8738.56
	6821.10	8742.11
	6821.53	8732.36
	6820.03	
Mean and std dev of mean	6820.05 ± 0.45	8734.20 ± 2.1

for succinonitrile and to the reaction below for triethylenediamine.

$$C_6H_{12}N_2(c) + 9O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l) + N_2(g)$$

Derived Results. Table IV lists the results derived from the experimental data at 298.15°K. The values of $\Delta E_c°$ and $\Delta H_c°$ are for the idealized combustion reactions delineated above. Other data are also used in the calculation of $\Delta G_f°$(c) for succinonitrile[6] and triethylenediamine.[8] Enthalpy of vaporization and vapor pressure data for succinonitrile[14] and triethylenediamine[15] are used in the evaluation of $\Delta H_f°$(g) and $\Delta G_f°$(g).

Table IV. Derived Thermodynamic Data (kcal mol^{-1}) at 298.15°K

Compound[a]	Succinonitrile	Triethylenediamine
For the Crystalline State		
$\Delta E_c°$(c)	−546.22 ± 0.10	−979.77 ± 0.86
$\Delta H_c°$(c)	−546.22 ± 0.14	−980.95 ± 0.86
$\Delta H_f°$(c)	33.38 ± 0.16	6.75 ± 0.88
$\Delta S_f°$(c)	−67.84 ± 0.05	−203.53 ± 0.05
$\Delta G_f°$(c)	53.61 ± 0.16	67.43 ± 0.88
For the Sublimation Process and Compression of the Vapor		
ΔH_s	16.73 ± 0.06[b]	14.8 ± 0.8[c]
ΔS_s	56.11 ± 0.21	49.6 ± 2
ΔS_{comp}	−22.86 ± 0.10	−14.9 ± 0.5
For the Ideal Gaseous State at 1 Atm		
$\Delta H_f°$(g)	50.11 ± 0.21	21.6 ± 1.6
$\Delta S_f°$(g)	−34.6 ± 0.28	−16.9 ± 2
$\Delta G_f°$(g)	60.4 ± 0.32	26.6 ± 2.6

[a] (c) and (g) refer to plastically crystalline and gaseous states, respectively. Precision indices are the recommended "uncertainty interval" which equals twice the final overall standard deviation of the mean. [b] A. L. Woodman, W. L. Murbach, and M. H. Kaufman, *J. Phys. Chem.*, **64**, 658 (1960). [c] T. Wada, E. Kishida, Y. Tomiie, H. Suga, S. Seki, and I. Nitta, *Bull. Chem. Soc. Jap.*, **33**, 1317 (1960).

Discussion

In an earlier determination, Parris, *et al.*,[4] reported values of $\Delta H_c°$(c) and the derived $\Delta H_f°$(c) for triethylenediamine at 298.15°K as −970.8 ± 2 kcal mol^{-1} and −3.4 ± 2.2 kcal mol^{-1}. This measurement was made with a static bomb calorimeter on a sample probably inadequately protected from atmospheric carbon dioxide and water; hence, less precise (and also less accurate) data would be anticipated.

Kharasch[3] reported a value for the combustion of succinonitrile which, upon adjustment with modern ancillary data,[16] corresponds to $\Delta H_f°$(c) = 33.23 kcal mol^{-1}, in good accord with the findings of this research.

The Strain Energy of Succinonitrile. Freedom of reorientation and diffusion of both triethylenediamine and succinonitrile in the "plastic crystal" phase has a profound effect on the thermodynamics of these molecules and especially on that of melting. In these materials, the disordering processes which characterize the transition from a crystalline material to a liquid may be subdivided into rotational–reorientational disordering which takes place at the transition to the plastic crystal phase and into complete positional disordering which alone takes place at the melting point. The entropy of the melting process, therefore, is relatively low, usually below 5 cal mol^{-1} °K^{-1}. The very propinquity of atoms which leads to the globular shape gives rise to energetic interactions between them. The magnitude of these interactions (*e.g.*, the strain energy) and identification of their origins may be deduced by comparison of the measured value of the enthalpy of formation [$\Delta H_f°$(g)] with that calculated by semiempirical methods.

$\Delta H_f°$(g) for succinonitrile may be calculated from bond energy schemes[17] as 46.3 kcal mol^{-1}. Comparison of this value with the experimental result of 50.1 kcal mol^{-1} reveals the presence of 3.8 kcal mol^{-1} of strain energy. This may be resident in angular distortions and energetic interactions occasioned by repulsion between the dipoles of the terminal nitrile groups. The suggestion gains support upon comparison of $\Delta H_f°$(g) for malononitrile and for glutaronitrile[16] calculated in the same way as that for succinonitrile. Because malono-,[16] succino-, and glutaronitrile have respectively one, two, and three methylene groups separating the terminal nitrile groups, strain due to angular distortion caused by CN interactions should decrease along the sequence. Strain energies of 12.2, 3.8, and −0.5 kcal mol^{-1} for malono-, succino-, and glutaronitrile confirm this prediction. Cyanogen, with no methylene groups between the nitrile groups,

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also has a low strain energy (about 0.5 kcal mol^{-1}), in further support of the origin of the strain in angular distortion. The calculations are summarized in Table V.

Table V. Strain Energies of Dinitriles at 298.15°K, kcal mol^{-1}

Compound	Formula	$\Delta H_f°$-(g)$_{obsd}$	$\Delta H_f°$-(g)$_{calcd}$	$[S]^c$
Cyanogen	NC–CN	73.84^a	73.6	0.2
Malononitrile	NC–CH_2–CN	63.5^b	51.2	12.2
Succinonitrile	NC–$(CH_2)_2$–CN	50.11	46.3	3.8
Glutaronitrile	NC–$(CH_2)_3$–CN	40.9^a	41.4	−0.5

[a] Reference 16. [b] Reference 17. [c] $[S] = \Delta H_f°(g)[\text{obsd} - \text{calcd}]$.

The Strain Energy of Triethylenediamine. This molecule has a cage structure akin to that of bicyclooctane. The structure constrains the methylene hydrogen atoms into the higher energy eclipsed conformation. Hendrickson[18] calculated by molecular mechanics that this strain is relieved in bicyclooctane by a slight twist of the molecule from the symmetric D_{3h} structure to the acentric D_3 structure. Other workers have suggested that the triethylenediamine molecule is similarly distorted. Although X-ray diffraction[19] and spectroscopic[19,20] studies have failed to reveal such a distortion, there is recent evidence from a quadrupole resonance experiment[21] that the molecule may indeed be slightly distorted.

The strain energy of triethylenediamine may be calculated by comparing the observed value of $\Delta H_f°(g)$ with that calculated by group increment or bond energy schemes. The group increment and the Allen and the Laidler schemes predict 10.8 kcal mol^{-1} for $\Delta H_f°(g)$ of triethylenediamine. The observed value for this quantity in Table IV (21.6 kcal mol^{-1}) should be diminished by $3RT$ (in which 3 is the number of rings in the compound) since a comparison of a cyclic compound with acyclic reference compounds is involved.[22] The strain energy of triethylenediamine, relative to a hypothetical acyclic reference compound, is then (in the gaseous state): $\Delta H_f°_{obsd} - 3RT - \Delta H_f°_{calcd} = 21.6 - 1.8 - 10.8 = 9.0$ kcal mol^{-1}.

Pitzer[23] has calculated the energy difference between the eclipsed and staggered conformations of ethane as 2.88 kcal mol^{-1}. If triethylenediamine is to be compared to a strain-free acyclic molecule, the three "eclipsed ethane" conformations must be allowed to relax to the staggered conformation. The energy release, about 8.6 kcal mol^{-1}, is significantly close to the predicted strain energy of the molecule (9.0 kcal mol^{-1}). It does not appear that there is significant strain release from this high-energy conformation, such as would occur if the molecule twists markedly.[23] Similar conclusions obtain for related bicyclooctane molecules.[5]

Acknowledgment. The authors are grateful to the Division of Research of the United States Atomic Energy Commission for support of this research endeavor. One of us (J. T. S. A.) thanks the University of Michigan for Rackham Predoctoral Fellowships; another (N. J. R.) thanks the National Science Foundation for a research participation award.

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A Semiempirical Investigation of π–σ Excitations in Nonplanar Hydrocarbons

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Abstract: The approximate intermediate neglect of differential overlap formalism for SCF calculations (INDO) developed by Pople, *et al.*, has been modified in order to (1) obtain relative orbital energies comparable to those obtained in nonempirical calculations and (2) reproduce, using a limited CI manifold, a reasonable ordering of the lower excited states for simple hydrocarbons. To obtain the first objective, it was necessary to give up hybridization invariance, while scaling down of the electron-repulsion integrals was also required to obtain the second. The resulting scheme seems to accommodate excitations among "tight" orbitals fairly well, but does not account for excitations to Rydberg-like orbitals. Calculations carried out on cyclooctatetraene, bicyclo[2.2.2]octatriene, and bicyclo[2.2.1]heptadiene indicate that transitions best described as CH → π^* and $\sigma \rightarrow \pi^*$ should be important in discussions of the near-ultraviolet spectra of these molecules. The conditions for the validity of the π-electron approximation are restated, and the possible consequences (in these calculations) of the INDO restrictions on the two-center electron repulsion integrals are discussed.

In attempting to account for spectral properties, one approach has been to treat nonplanar and nonconjugated unsaturated hydrocarbons as coupled ethylenic units, with no consideration given to any effects arising from nonorthogonality of orbitals designated π and σ in the limit of infinite separation. The success of this