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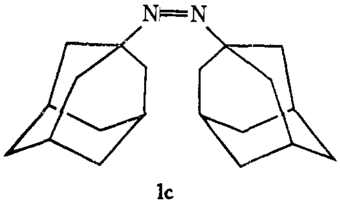
Stable Cis Dialkyldiazenes (Azoalkanes): *cis*-Di-1-adamantyldiazene and *cis*-Di-1-norbornyldiazene

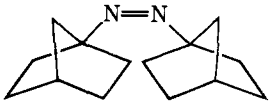
Sir:

Whereas cis aromatic diazenes (*cis*-ArN=NAr) have been known since 1937,[1] their aliphatic counterparts were discovered only in 1964.[2] The cis isomer of diisopropyldiazene is especially well characterized[3] but other cis diazenes which form more stable incipient radicals lose nitrogen rapidly at ambient temperatures.[4,5] In contrast, cis aryldiazenes only isomerize to trans,[6] although both pathways can be found in mixed aryl-alkyl cases.[7]

We were intrigued by the possibility that a properly chosen cis aliphatic diazene might isomerize to trans without losing nitrogen.[8] Trans compounds with considerable steric bulk and high energies of activation for decomposition were selected for study, with the expectation that the corresponding cis forms would be forced to isomerize thermally to trans. *trans*-Di-1-adamantyldiazene (**1t**) and di-1-norbornyldiazene (**2t**, Table I) meet both of these criteria and indeed, cis isomers **1c** and **2c** were found to behave in the anticipated manner, as summarized herein.



1c



2c

Table I. Activation Parameters for Thermolysis of Trans Diazenes

Compound	$\Delta H_{dec}^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	k_{rel}, 300°
Di-1-adamantyldiazene[9] (**1t**)	60.7	31.4	2×10^{-4}
Di-1-norbornyldiazene[10] (**2t**)	53.8	9.0	1×10^{-6}
Di-*tert*-butyldiazene[11] (**3t**)	42.2	16.2	1.0

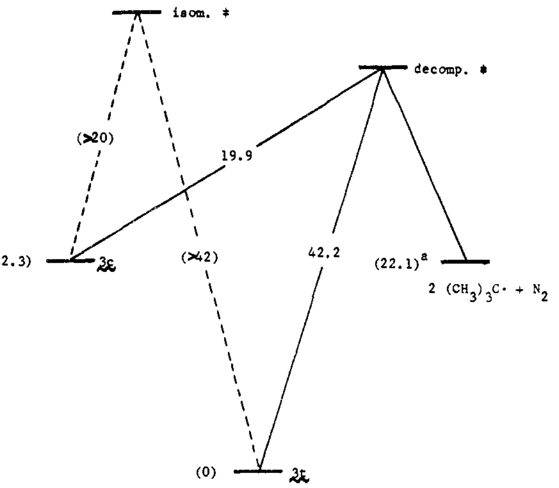


Figure 1. Enthalpy of di-*tert*-butyldiazene (**3**) and the transition states for isomerization and decomposition. Values in parentheses are assumed or calculated. Dashed line indicates a process not observed. [a] $2\Delta H_f[(CH_3)_3C\cdot] - \Delta H_f(\mathbf{3t})$.

Uv irradiation of **1t** in toluene at 0° produced an intense yellow color (**1c**) which faded slowly on warming to room temperature. Its disappearance was monitored at several temperatures on a Cary 17, giving the activation parameters shown in Table II. Compound **2t** behaved similarly except that much higher temperatures were required to cause fading of the color. The greater stability of **2c** allowed its isolation by chromatography on basic alumina, yielding yellow needles which melted at 92.5-93.5°. Further heating (100-115°) in the capillary tube transformed the yellow liquid into a white solid, which remelted at 165-166°. (Authentic **2t** melted at 166-167°.) The sharp melting point implies that little decomposition of **2c** occurs on heating, and is consistent with the extremely low quantum yield for loss of nitrogen (cf. Table II) from **2t.** The quantum yield is higher in the case of **1t,** but still far below the 0.46 reported for **3t.**[12]

Interpretation of the above results is facilitated by first examining the energetics of **3** (cf. Figure 1). The difference between $\Delta H_{dec}^{\ddagger}$ of **3t** and **3c** (22.3 kcal mol^{-1}) is taken as the ground state energy of **3c,** based on the assumption that **3c** and **3t** have transition states of similar energy.[5,13] Since **3c** decomposes rather than isomerizing, the transition state for the latter process must lie above 42 kcal mol^{-1} on the diagram, neglecting possible $\Delta S^{\ddagger}$ differences.

The energy diagram for **2** is shown in Figure 2. A preliminary measurement by differential scanning calorimetry gave a value for the enthalpy of isomerization **2c**(s) → **2t**(s) of approximately 12 kcal mol^{-1},[14] which will be assumed to equal the gas phase value.[15] Despite the slight uncertainty in this measurement, it is clear that isomerization of **2c** is favored over decomposition by ~10 kcal mol^{-1}. In view of the bulky groups in **2c,** its strain energy relative to **2t** (12 kcal mol^{-1}) is intuitively reasonable when compared with *cis*-diisopropyldiazene, which possesses 8 kcal mol^{-1} of

Table II. Data for Diazenes **1-3** in Hydrocarbon Solvents

Compound	λ_{max}, nm				
	Trans	Cis	ΦN_2[a]	$\Delta H^{\ddagger}$, kcal mol^{-1} [c]	$\Delta S^{\ddagger}$, eu[c]
Di-1-adamantyldiazene (**1**)	368	455	<0.004	25.9 ± 0.5	13.4 ± 1.6
Di-1-norbornyldiazene (**2**)	364	423	0.0008[b]	31.8 ± 0.4	12.8 ± 1.2
Di-*tert*-butyldiazene (**3**)	368	447	0.46	19.9 ± 0.4[d]	4.3 ± 1.5[d]

[a] Quantum yield for nitrogen formation from trans isomers. [b] The irradiated solution was heated for 6 min at 100° before measuring N_2 yield. [c] Activation parameters for disappearance of cis compound. [d] Reference 5.

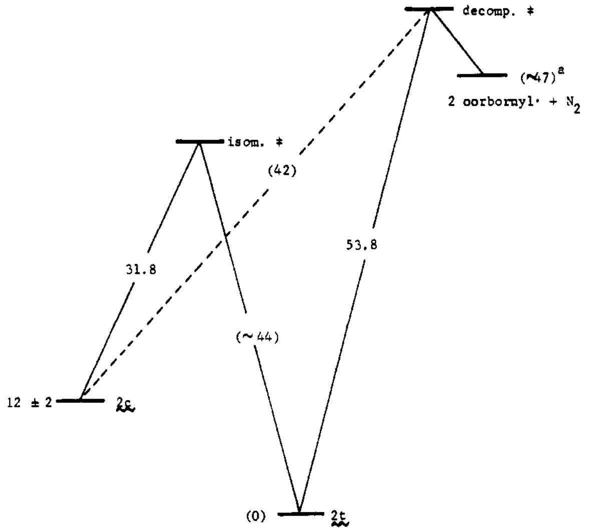


Figure 2. Enthalpy of di-1-norbornyldiazene (**2**) and the transition states for isomerization and decomposition. See caption for Figure 1. ^{a} Estimated.

strain.[5,16] Furthermore, it will be noted in Table II that λ_{max} for **2c** lies between the 380 nm found for *cis*-diisopropyldiazene and the 447 nm for **3c.** It has been proposed that λ_{max} is a function of N–N–C bond angle,[17] which in turn should govern the strain energy.[16] In fact, the strain energy of **2c** is intermediate between that of *cis*-diisopropyldiazene and **3c.** We therefore have a self-consistent picture in which the lower strain in **2c** relative to **3c** coupled with the higher $\Delta H_{dec}^{\ddagger}$ of **2t** (lower stability of incipient radical) combine to make decomposition of **2c** energetically inaccessible.

1 resembles **2** in its low quantum yield of nitrogen but the λ_{max} of **1c,** which is the longest ever found for an acyclic cis diazene, is not far from that of **3c.** Its strain energy probably lies in the region of 24 kcal mol^{-1}, which places the transition state for isomerization at 50 kcal mol^{-1}. Since some nitrogen is evolved on heating **1c,** the transition state for decomposition must not be much above 50 kcal mol^{-1}. This figure is considerably lower than the reported $\Delta H_{dec}^{\ddagger}$ of **1t** (cf. Table I), a value quite possibly in error.[18]

A final note concerns the effect of ground state energies of cis diazenes on $\Delta H^{\ddagger}$ of isomerization. *cis*-Diisopropyldiazene possesses 8 kcal mol^{-1} of strain and $\Delta H_{isom}^{\ddagger}$ is 32.3 kcal mol^{-1}. Both cis diazenes studied here are more strained than *cis*-diisopropyldiazene and also have lower values of $\Delta H_{isom}^{\ddagger}$. Although variations in $\Delta S_{isom}^{\ddagger}$ make quantitative arguments tenuous, it is gratifying to note that the very strained **1c** isomerizes more readily than the less strained **2c.**

These results then, allow one to predict when stable cis dialkyldiazenes might be isolable, namely, when decomposition is impeded by radical instability and when isomerization is not facilitated by bulky substituted groups.

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Thermochemistry of Cyclic 1,2-Dialkyldiazenes (Azo Compounds). The Effect of Strain Energy on Thermal Lability

Sir:

Despite the potential utility of thermochemical data in understanding the decomposition of 1,2-dialkyldiazenes,[1] their heats of formation (ΔH_f) have seldom been measured. Prior to 1973, most ΔH_f's for these compounds were estimated from Coates and Sutton's early study of diisopropyldiazene (**1**);[2] however, more recent work[3] showed their value to be in error by nearly 11 kcal mol^{-1}.

The present report deals mainly with ring strain in cyclic diazenes but it also includes new data[4] on di-*tert*-butyldiazene (**2**), whose first reported[3] ΔH_f was unexpectedly low. Moreover, the present enthalpies of vaporization (ΔH_v) were determined by vaporization calorimetry[6] and are considerably more accurate than those measured earlier.[3]

Strain energies are calculated by comparison of specific pairs of compounds. For all cases in which the α-carbon atom is fully substituted, **2** is taken as the reference compound; however, in the case of **5**, diisopropyldiazene (**1**) is a more appropriate model. A sample calculation of the strain energy of **4** is given below, using group contributions taken from the compilation of Benson and O'Neal.[7] For **2**: $\Delta H_f = -8.51 = 6[\text{C-(C)(H)}_3] + 2[\text{C-(C)}_3\text{(N)}] + [\text{-N=N-}]$. Since $[\text{C-(C)(H)}_3] = -10.08$, it follows that $2[\text{C-(C)}_3\text{(N)}] + [\text{-N=N-}] = 51.97$. For **4**: ΔH_f (calcd) $= 2[\text{C-(C)}_3\text{(N)}] + [\text{-N=N-}] + 4[\text{C-(C)(H)}_3] + 2[\text{C-(C)}_2\text{(H)}_2] = 51.97-40.32-9.90 = 1.75$ kcal mol^{-1}. Strain $= \Delta H_f$ (obsd) $- \Delta H_f$ (calcd) $= 10.03 - 1.75 = 8.28$ kcal mol^{-1}.

Table II summarizes the strain energies thus calculated.[8] Part of the 2.7-15.4 kcal mol^{-1} strain in these compounds must be due to the energy difference between the cis and trans diazene linkage. Although it is now clear that the cis is normally of higher energy,[9] the magnitude of the cis-trans difference remains unmeasured. It is suggested here