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is due to a decrease of the rate constant k_{nr} in that order (Table IV) and is probably connected to the energetic lowering of the initial state E^* of the bridged compounds (compare the red-shifted absorption, Table I) which will decrease k_{EP}. This relative energy lowering of the E^* state can also explain the "normal" decreasing lifetime above 77 K before the A^* state is reached, as observed for the group 1 derivatives.

The state P^* is not available for DS-B34 (group 3) and the lifetime and the quantum yield of fluorescence are only weakly affected by the temperature and the solvent polarity. As a matter of fact the slight increase of the lifetime at around 160 K in ethanol and at 230 K in ether is in favor of an equilibrium between two emitting states (E^* and A^*).

The intramolecular fluorescence quenching rate constant, k_{nr}, measured at 223 K shows very clearly that the main deactivating step is the formation of P^* connected with the rotation of the double bond ($k_{nr} \approx 0$ for DS-B34 and $k_{nr} \geq 9500.10^7$ s^{-1} for DS-B2 in EtOH). If the bridging bond in DS-B2 is taken away leading to increased molecular flexibility, the TICT state can be populated and k_{nr} is reduced by nearly two orders of magnitude ($k_{nr} = 72 \times 10^7$ s^{-1} in EtOH for DS). This provides a further example of a stabilization (lifetime lengthening) of the emitting excited state due to an increase of the dimensionality of the reaction hypersurface, which would be unexplainable by a two-state model.[8] On the other hand, if the dimensionality is affected by bridging a bond not connected to TICT formation (e.g. bond 4), the k_{nr} values are unaffected (compare DS and DS-B4 in Table IV, both of group 2). The k_{nr} rate constant decreases moderately with an increase of the solvent polarity, showing that E^* and A^* are more polar than the quenching state P^*.

Compound X (DDS) with an additional dimethylamino group with respect to DS excells by its tenfold increased quantum yield although the absorption and fluorescence properties are rather similar (Table I). From the temperature dependence of the lifetimes (Table III) it may be calculated that there remains a residual quenching pathway k_{nr}. If it is attributed to quenching by P^*, then the small k_{nr} values with respect to DS and DCS[7-9] may be explained by two factors: (i) the energy of P^* is raised relative to E^* in donor-donor-stilbenes (DDS) as compared to donor-stilbenes (DS) and donor-acceptor-stilbenes (DCS). Quantum chemical calculations to answer this point are underway; (ii) DDS may also populate a TICT (A^*) state and thus energetically stabilize the original E^* state by an excited state equilibrium. This view is supported by the fairly large excited-state dipole moment observed (Table II) although the compound is symmetric, and small dipole moments for both ground and excited state are expected. Further studies including bridged DDS model compounds may help to answer this question.

This study extends the results previously obtained for the DCS series.[7-9] All results can be explained within the same three-state model and provide additional evidence for the extensive importance of the single bond twist mechanism in polar arylethylene derivatives.

Acknowledgment. This work has been supported by BMFT project 05 414 FAB1 and the EC-Large Scale Installations Program (GE 1-0018-D(B)). We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial assistance and T. Wolff, University of Siegen, for a sample of DS-B34.

Bond Dissociation Energies of 3,5,5- and 4,5,5-Trimethyl-2-oxomorpholines by Photoacoustic Calorimetry. An Assessment of the Additivity of Substituent Effects[1]

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Abstract: Carbon-hydrogen bond dissociation energies (BDE) and absolute rate constants for hydrogen atom abstraction by the *tert*-butoxyl radical have been measured for a number of aliphatic amines, including two captodatively substituted compounds (4,5,5-trimethyl-2-oxomorpholine (**1**) and 3,5,5-trimethyl-2-oxomorpholine (**2**)). The bond energies, determined by photoacoustic calorimetry, cover a range of about 15 kcal mol^{-1} (ca. 90 kcal mol^{-1} for the aliphatic amines to 75 kcal mol^{-1} for 4,5,5-trimethyl-2-oxomorpholine). The reactivity of the C-H bonds with the *tert*-butoxyl radical illustrates the importance of the stereoelectronic effect: in this case, conjugation between the incipient radical center and the developing π-system. In addition, there is evidence suggesting that relief of ring strain also plays an important role in determining both the BDE and the reactivity of the amine. The estimation of the captodative stabilization energies of the title compounds from BDE data is difficult for a number of reasons. The usual assumption that relative BDE(C-H) values are a measure of relative radical stabilization energies (RSE) is questioned. For cyclic esters evidence suggests that strain effects on the hydrocarbon versus those on the radical may have a significant effect. In addition, we have shown that the addition of RSE's from a methane based scale will overestimate the combined effect of two substituents on a C-H bond. We conclude that the method proposed originally by Benson provides a better estimate of multiple substituent effects on the BDE's. The analysis of the BDE's using this approach leads us to the conclusion that, for **1**, the substitutent effects on BDE(C-H) appear to be synergetic by ca. 9 kcal mol^{-1}. This should not be interpreted as a measure of the captodative effect on the radical since it is difficult to estimate the extent to which the relief of ring strain influences the BDE.

One of us has reported that the radicals 3,5,5-trimethyl-2-oxomorpholin-3-yl (TM-3) and 4,5,5-trimethyl-2-oxomorpholin-3-yl (TM-3′) exist in equilibrium with their respective dimers, at ambient temperatures, with steady state concentrations that are observable by EPR.[2-7] The C-C bond dissociation energies (BDE's) of the TM-3 and TM-3′ dimers in ethanol are 20.4 and

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[†] National Research Council of Canada.
[‡] University of Colorado.

(1) Issued as NRCC publication No. 35241.

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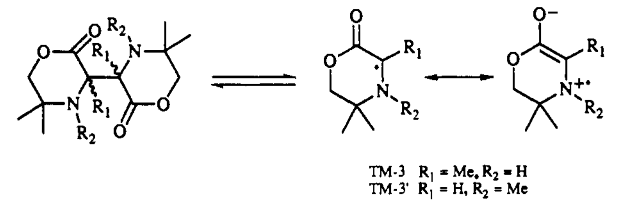
Scheme I



26.4 kcal mol^{-1}, respectively.[7] The unusual thermodynamic properties of the dimers have been attributed, in part, to stabilization of the radical center by the interaction of the two substituents of opposite electron demand. This synergetic interaction has variously been called the captodative effect,[8] merostabilization,[9] or push-pull stabilization (Scheme I).[10] The magnitude of this effect has been the subject of experimental and theoretical investigation for a number of years.[11]

Variations in the BDE(C–C) are not simply a reflection of the relative stabilities of the radical but also reflect changes in steric and electronic effects in the dimer.[12] This is clearly demonstrated by the BDE(C–C) values for the dimers of TM-3′ (26.4 kcal mol^{-1}) and 4-ethyl- (24.8 kcal mol^{-1}) and 4-(2-propyl)-2-oxomorpholin-3-yl (19.4 kcal mol^{-1}) radicals.[7] In this case, increasing the degree of alkylation of the *N*-alkyl group resulted in a decrease in the BDE even though the electronic effect on the stability of the radicals was expected to be essentially constant. Recent work by Bordwell[13–18] and Pasto[19] has suggested that comparison of BDE(C–H) values is preferred. In this approach relative stabilization energies (RSE) of radicals are equated to the ΔBDE of the corresponding hydrocarbon with the BDE of methane (105 kcal mol^{-1}) chosen as the standard. The RSE of a disubstituted radical XYCH$^\bullet$ is compared to the sum of RSE(XCH$_2^\bullet$) and RSE(YCH$_2^\bullet$) to determine if the effects are additive, synergetic, or antagonistic. Bordwell makes the reasonable suggestion that the absence of a saturation effect (i.e. additivity) is evidence for a captodative effect of *at least* 5 kcal mol^{-1}.[13]

In this paper we report the BDE(C–H) for 4,5,5-trimethyl-2-oxomorpholine (**1**), 3,5,5-trimethyl-2-oxomorpholine (**2**), as well as a number of related model compounds measured by laser induced photoacoustic calorimetry. In addition, the reactivities of these compounds with the *tert*-butoxyl radical have been measured by laser flash photolysis. The relevance of these measurements to understanding the electronic and stereoelectronic effects in the bond homolysis reactions is discussed.

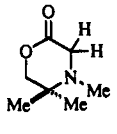
Table 1. C–H Bond Dissociation Enthalpies and Rate Constant for Hydrogen Abstraction by *tert*-Butoxyl Radical in Benzene

substrate	BDE (kcal mol^{-1})[a]	$k_{abs} \times 10^{-7}$ (M^{-1} s^{-1})[b]	$k_{abs}/H \times 10^{-7}$ (M^{-1} s^{-1})[c]
1	75.3	28	25
2	77.5	11	11
3	82.1	8.5	5.5[i]
4	84.1	12	9[i]
5	79–83[d]	9.5	1.5
6	*e*	<0.2	<0.1
7	77[f]		
8	78[f]		
trimethylamine	87.5	10[h]	1.1
morpholine	90.8	4.1	1.0
piperazine	89.5	11.4	1.4
δ-valerolactone	89[g]		

[a] Measured by photoacoustic calorimetry in benzene; the errors on the BDE's are ±2.3 kcal mol^{-1}. The errors in α_{obs} and Φ were ±0.02 and ±0.05, respectively. The value of ΔV_1 used for the volume correction (see text) was 12.6 ± 2 cm^3 mol^{-1}. [b] All values ±10%. Measured by laser flash photolysis using diphenylmethanol as a probe. The rate constant for **1** also was determined by direct observation of the radical absorption. [c] Rate constant per hydrogen which is defined as the molecular rate constant (column 2, corrected for reaction with the *N*-methyl groups) divided by the number of available hydrogens. We have assumed that only the axial hydrogen of **1** is reactive and that the reactivity of the *N*-methyl groups is the same per hydrogen as that for trimethylamine. [d] Lower and upper limits based on the estimated selectivity by laser flash photolysis (lower) or EPR spectroscopy (upper) and the measured average value 84.7 ± 2.3 kcal mol^{-1} (ref 32). [e] The rate was too slow to obtain a reliable BDE. [f] From Bordwell and coworkers, ref 15. [g] Based on the estimated BDE(C–H) in ethyl acetate (95 kcal mol^{-1}, ref 17), and the assumption that the bond energy difference between acetone and cyclohexanone (6 kcal mol^{-1}, Bordwell, F. G.; Harrelson, J. A., Jr. *Can. J. Chem.* **1990**, *68*, 1714) is the same as that between ethylacetate and the lactone. [h] Reference 28. [i] The correction for abstraction from the *N*-ethyl group is based on a reactivity per hydrogen of 1.5 × 10^7 M^{-1} s^{-1}.

Results and Discussion

Photoacoustic Calorimetry. Bond enthalpies were determined by photoacoustic calorimetry for **1–6** as well as for morpholine, piperazine, and trimethylamine (Table I). This technique is described in detail elsewhere.[20–22] Briefly, an argon-saturated



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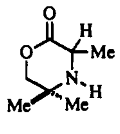

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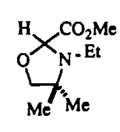

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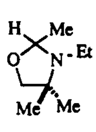

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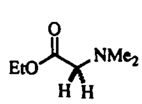

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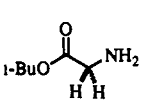

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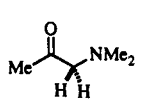

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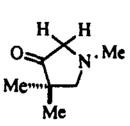

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benzene solution of the substrate and di-*tert*-butyl peroxide (1–12%, v/v) was photolyzed using a pulsed nitrogen laser (337.1 nm, 84.8 kcal mol^{-1}, eqs 1–3). The excess heat from the overall reaction, eq 3 (i.e. ΔH for the reaction subtracted from the photon energy), produced a shock wave that was detected using a piezoelectric transducer in contact with the bottom of the cell. The intensity of the shock wave is linearly proportional to the amount of heat evolved (provided that all of the chemistry is completed within 100 ns; i.e. k_2[RH] > 10^7) and the overall volume change for the conversion of reactants to products.[23] To ensure that the

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kinetic criterion is met, the rate constants for the hydrogen abstraction from each substrate by the *tert*-butoxyl radical were measured by laser flash photolysis. These kinetic data also are given in Table I along with some relevant data reported by Bordwell and his co-workers.[15]

$$t\text{-BuOOBu-}t \xrightarrow{h\nu} 2\,t\text{-BuO}^{\bullet} \tag{1}$$

$$\underline{2\,t\text{-BuO}^{\bullet} + 2\,\text{RH} \rightarrow 2\,t\text{-BuOH} + 2\,\text{R}^{\bullet}} \tag{2}$$

$$t\text{-BuOOBu-}t + 2\,\text{RH} \rightarrow 2\,t\text{-BuOH} + 2\,\text{R}^{\bullet} \tag{3}$$

In our experiments, the photoacoustic shock wave was calibrated using *o*-hydroxybenzophenone as a standard, which returns all of the absorbed energy to the medium as heat in less than 1 ns. Thus, it is possible to determine the fraction of the absorbed light energy that is converted to heat, α_{obs}. This fraction is actually the sum of two terms (eq 4, $\chi_s = (\beta\cdot\text{MW})/(\rho\cdot C_p)$ where β is the volume expansion coefficient, MW is the molecular weight, ρ is the density and C_p is the heat capacity of the solvent,[24] and $h\nu$ is the photon energy):[23] one which is related to the volume change that results from the deposition of the residual heat from reaction 3, α_{th} (i.e. thermal expansion), and one which is related to the volume change of the reaction itself, ΔV_3. Since it is the term α_{th} that is required to determine the bond energy (eqs 5 and 6 where Φ is the quantum yield for the photolysis of di-*tert*-butyl peroxide) it is necessary to estimate ΔV_3 for reaction 3.

$$\alpha_{\text{obs}} = \alpha_{\text{th}} + \frac{\Delta V_3 \Phi}{\chi_s h\nu} \tag{4}$$

$$\Delta H_3 = \frac{h\nu}{\Phi}(1 - \alpha_{\text{th}}) \tag{5}$$

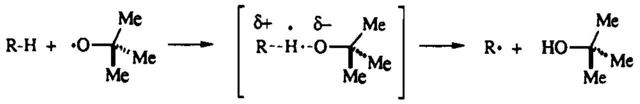
$$\text{BDE} = \frac{\Delta H_3}{2} + 85.1 \tag{6}$$

The value of ΔV_3 is expected to be similar to the volume change for the homolysis of the di-*tert*-butyl peroxide (ΔV_1) since the volume change of reaction 2, where the number of bonds in reactants and products are the same, is expected to be small.[25] Work by Walling and Metzger[26] provides a lower limit for ΔV_1 in benzene of 12 ± 2 cm^3 mol^{-1}. Preliminary work in our laboratory is consistent with this value. In benzene, if the effect of volume change is not considered, a value of $\alpha_{\text{th}} = 0.664 \pm 0.021$ is obtained from a photoacoustic experiment, leading to an apparent value of Φ of 0.75 ± 0.03. If, however, the volume change is included (χ_s(benzene) = 3.30 cm^3 kcal^{-1}) a value of 0.85 ± 0.04 is obtained. The latter value is in agreement with that expected from the cage effect as a function of viscosity for this reaction.[27] It is important to point out that the effect of ignoring this volume change is to underestimate the BDE by 2.1 kcal mol^{-1}. The BDE values in Table I include the correction for the volume change. However, it should be pointed out that the difference of 2.1 kcal mol^{-1} is within the 95% error limits of our measurements of ±2.3 kcal mol^{-1}.

Kinetics for the Reactions of 1 and 2 with *tert*-Butoxyl. The rate constants for hydrogen atom abstraction from **1** by the *tert*-butoxyl radical were measured by direct spectroscopic observation of the radical which had a broad absorption between 300 and 350 nm. An apparent maximum at 310 nm was, in fact, an experimental artifact which resulted from bleaching of the absorption of the precursor. Rate constants for **2** and the other aliphatic amines in Table I were determined using diphenylmethanol as a probe.[28] Both methods gave the same rate constant for the reaction with **1**. Product studies confirmed that the selectivity of the *tert*-butoxyl radical toward C_3–H was >90%.

The kinetics of hydrogen abstraction by *tert*-butoxyl radical are known to be influenced by polar and stereoelectronic factors.[28-31] Griller and co-workers found that the reactivity increased in the order primary < secondary < tertiary with hydrogen atom abstraction from tertiary amines being ca. 3–5 times faster than primary amines per hydrogen.[28] For ethers[29] and amines[28] the rate constants increased as the dihedral angle between the C–H bond and π-system of the developing radical decreased. In addition, Malatesta and Ingold suggested that relief of ring strain also can lead to rate accelerations.[30] The data in Table I provide evidence for similar stereoelectronic effects. The last column in this table represents the rate constant *per hydrogen*, i.e. the observed molecular rate constant divided by the number of available hydrogens. In cases where more than one type of hydrogen is available (i.e. abstraction from *N*-methyl) the rate constant per hydrogen is corrected using the assumption that the reactivity of the *N*-methyl group is the same as that for trimethylamine (1.1 × 10^7 M^{-1} s^{-1} per hydrogen).

Scheme II



Cyclic compounds **1–4** show enhanced reactivity toward *tert*-butoxyl compared to the acyclic aminoester, **5**, and the other aliphatic amines. In the case of **5** the reactivity per hydrogen of the methylene is the same as the reactivity of the methyl group.[32] The increased reactivity of **1** and **2** compared to **5** can be attributed to the favorable alignment of the C–H bond in these rigid compounds. Furthermore, considerable relief of ring strain is expected upon C–H homolysis in these highly substituted systems. In an effort to obtain a more accurate BDE determination for an acyclic compound, we attempted to measure the BDE(C–H) of **6**. Unfortunately, photoacoustic measurements were precluded in this case because this compound was too unreactive toward the *tert*-butoxyl radical (Table I). The decrease in reactivity is consistent with the difference between primary and tertiary amines and is associated with a stereoelectronic effect. If relief of ring strain is an important consideration, some evidence of this may be observable in the thermochemistry of these reactions (see below).

Multiple substitution at the incipient radical center complicates the interpretation of the relative rates since there are two other factors that will have a significant influence. In addition to the stereoelectronic effect, the rates will be attenuated by the overall exothermicity (Hammond Postulate) and electronic effects associated with the transition state (i.e. the polar effect). For the latter, electron withdrawing groups tend to decrease the rate while electron donating groups tend to increase the rate (Scheme II). As a result, in the case of the amino esters versus the aliphatic amines, the increased exothermicity will tend to increase the rate

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(32) Hydrogen atom abstraction from **5** by the *tert*-butoxyl radical was not highly selective. As a result, the apparent bond energy of 84.7 kcal mol^{-1} is actually a weighted average: $\text{BDE}_{\text{obs}} = f\cdot\text{BDE(methylene)} + (1 - f)\cdot\text{BDE(methyl)}$, where f is the fraction of abstraction that occurs at the methylene. Attempts were made to define the selectivity in **5** more precisely. An electron spin resonance spectrum at 25 °C (0.15 M of **5**, 0.15 M di-*tert*-butylperoxide in benzene) was a mixture of two radicals but was clearly dominated by abstraction from the methylene (a_H(CH) = 11.1 G, a_N = 8.2 G, a_H(CH$_3$) = 7.2 G, a_H(CH$_3$) = 6.8 G). A less intense spectrum of a second radical at lower *g* (presumably from abstraction from the methyl group) was more difficult to analyze. If it is assumed that the rates of radical–radical combination are the same for the two radicals then a selectivity of between 2:1 and 3:1 in favor if methylene abstraction over methyl abstraction is obtained. Using a selectivity of 2:1 (f = 0.67) and an assumed BDE (CH$_3$) of 87 kcal mol^{-1} (i.e. the same as that in trimethylamine) the BDE(CH$_2$) is determined to be 83.5 kcal mol^{-1}. If, however, it is assumed that the rate constant per hydrogen for abstraction from the methyl group of **5** is the same as that for trimethylamine (1.1 × 10^7 M^{-1} s^{-1}) then the selectivity toward the methylene is estimated to be 0.3. This leads to the lower limit of 79 kcal mol^{-1} in Table 1.

while the destabilization of the polar transition state by the electron withdrawing group will tend to decrease the rate. How these effects will balance is difficult to predict. Not surprisingly, while there is a trend, an Evans–Polanyi type plot of log(k_2) versus BDE is scattered. We note in this regard that the reaction of **3** with *tert*-butoxyl is slower than the reaction of **4** even though the bond being broken is 3 kcal mol^{-1} weaker. In the reaction of **4**, the transition state is stabilized by three donor groups.

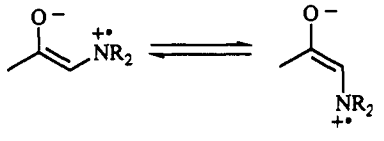
Thermochemistry. A number of interesting observations are apparent from the BDE data in Table I. The BDE's determined for the simple aliphatic amines are consistent with those reported in the literature.[33,34] The BDE's of **1** and **2** are ca. 15 kcal mol^{-1} weaker than the more simple amines. The question of whether or not the substituent effects are additive is addressed in a separate section below. The C–H bond in **1** is apparently weaker than the bond in **2**, even though alkylation at the incipient radical center generally results in bond weakening of 1–5 kcal mol^{-1}. One may argue that the BDE values are the same within the experimental relative error (±2 kcal mol^{-1}); however, clearly, the bond in **2** is not significantly weaker than the bond in **1**. We tentatively suggest that a greater relief of ring strain in **1** compared to **2** upon C–H bond homolysis is responsible for this difference. In the case of **2** the methyl at C_3 occupies the equitorial position thus avoiding steric interaction with the *gem*-dimethyl at C_5. On the other hand, in **1** there must be steric interaction between the methyl groups, and the ring strain will increase in order to achieve a conformation in which the *N*-methyl group bisects the *gem*-dimethyls on C_5. Some support for this suggestion is obtained from molecular mechanics calculations (MM2 force field)[35] which indicate that the strain energy (SE) in **1** is 11.2 kcal mol^{-1} while that in **2** is only 5.7 kcal mol^{-1}. The variation in bond energies due to differences in the relief of ring strain upon formation of radicals has the important implication that the relative C–H bond energies may not reflect, simply, differences in the radical stabilities.

The estimated BDE of **5** supports the suggestion that strain energy differences are important in understanding relative BDE's (Table I). In this case, since the abstractions of both the methyl and the methylene hydrogen atoms are fast on the photoacoustic time scale, an average bond energy of 84.7 kcal mol^{-1} was obtained experimentally. Deriving the BDE of the methylene from the measured selectivity and the measured BDE of trimethylamine is straight forward (i.e. a simple weighted average) but leads to a larger relative error.[32] Our derived upper and lower limits are 83 and 79 kcal mol^{-1}, respectively, and compare well with the value determined by Bordwell for **7** of 77 kcal mol^{-1} (Table I).[13] The larger BDE compared to **1** undoubtly reflects differences in the strain energy and stereoelectronic effects.

While the ΔBDE of morpholine versus **1** or **2** is ca. 15 kcal mol^{-1}, that for **4** versus **3** is only 2 kcal mol^{-1}. A number of factors will contribute to this rather large difference. The radical derived from **3** has the ester function exocyclic to the ring. As a result, steric interactions can prevent the group from achieving an optimum conformation for overlap with the radical center. In addition, saturation effects in a trisubstituted radical are likely to be more important than in the disubstituted radicals.[13] Finally, strain energy differences between **3** and **4** (as well as their respective radicals) will likely be small. Less stabilization in the radical derived from **3** is consistent with the observed stability of its dimer, bi(2-carbomethoxy-3-ethyl-4,4-dimethyl-1,3-oxazolidin-2-yl) (see Experimental Section).

On the Additivity of Substituent Effects. The question of additivity of substituent effects for di- and trisubstituted radicals has been the subject of numerous investigations.[11,13-15,17,36] We have suggested that the unusual thermodynamic properties of the TM-3 and TM-3′ dimers are, in part, a consequence of synergetic interactions between the electron withdrawing carbonyl group and the electron donating amino group (i.e. the captodative effect, Scheme I).[2-5,7] One might expect that given BDE's for an appropriate set of model compounds, such as those in Table I, it should be simple to obtain (at least) a semiquantitative estimate of the magnitude of this effect.

Scheme III



Bordwell has estimated BDE's of a similar set of amino ketones using thermochemical cycles and suggested that the synergetic interactions depend on steric interactions in the radical[14] as well as the radical conformation.[36] It was suggested that the (*Z*) isomer of a captodatively substituted radical is instrinsically more stabilized than the (*E*) isomer as a result of the electrostatic interactions between the partially negative oxygen and partially positive nitrogen (Scheme III). However, the electrostatic interaction energy for the (*Z*) and (*E*) radicals in Scheme III, estimated to be 1.7 and 1.1 kcal mol^{-1}, respectively,[37] is smaller than the estimated ΔBDE.

Our data are not consistent with this explanation. We believe that it is, in fact, the cyclic nature of the **1** and **2** that contributes both to their unusually low BDE's and unusually high reactivity toward the *tert*-butoxyl radical (see above). Compounds **1** and **2** which are locked in the (*E*) conformation have lower bond energies than **5** which should be able to adopt the thermodynamically more favorable conformation. We suggest that the strain energy differences upon C–H homolysis are primarily responsible for the observed BDE differences between **1** and **5**.

The efficacy of using BDE data to estimate the additivity of radical stabilization effects has been questioned by a number of workers.[11] Rüchardt suggested that the changes in the strain energy in the hydrocarbon with its intact bond may contribute to the relative BDE's.[38] Nicholas and Arnold[39] argued that the C–X BDE should depend on the electronegativity of X. Recently, we have measured C–Br BDE's of a number of para-substituted benzyl bromides.[21] The variation of the BDE was surprisingly large for a remote substituent effect and provided further experimental support of the argument of Nicholas and Arnold. Nevertheless, it seems reasonable that, since C–H bonds are not polar, ΔBDE(C–H) values should reflect the RSE's.

Bordwell and his co-workers have used relative bond energies of model compounds to predict the BDE's of a number of hydrocarbons.[13-17,36,40-42] The relative BDE's were assumed to be a measure of the RSE using methane as the standard (BDE = 105 kcal mol^{-1}). They concluded that even additive substitutent effects are evidence for synergetic interactions since the multiple effects are expected to lead to a saturation phenomenon.[13] If this approach is applied to **1**, then the predicted RSE is 30.2 kcal mol^{-1}; i.e. the sum of the RSE for morpholine (105 − 90.8 = 14.2 kcal mol^{-1}) and that for δ-valerolactone (105 − 89 = 16 kcal mol^{-1}). This leads to a predicted bond energy of ca. 74.8 kcal mol^{-1} which compares well with the measured value of 75.3 kcal mol^{-1}.

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(33) Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* **1981**, *103*, 1586–1587.

(34) Burkey, T. J.; Castelhano, A. L.; Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* **1983**, *105*, 4701–4703.

(35) Serena Software In Bloomington, IN.

(36) Bordwell, F. G.; Cheng, J. *J. Am. Chem. Soc.* **1991**, *113*, 1736–1743.

(37) The interaction energy between two point charges, E_c, can be calculated using: $E = [(3.32 \times 10^4)Z_1Z_2f]/\epsilon r$ kcal mol^{-1}, where Z is the charge, ϵ is the dielectric constant, r is the interatomic distance in pm, and f is a term that depends on the ionic strength of the solution (f = 0.6 for a 0.1 M electrolyte solution). The interatomic distances were estimated to be ca. 2.5 Å for the (*Z*) isomer and 3.8 Å for the (*E*) isomer using molecular modeling. For a radical in DMSO with 0.1 M electrolyte the electrostatic binding energy is expected to be ca. 1.7 kcal mol^{-1} for the (*Z*) isomer and 1.1 kcal mol^{-1} for the (*E*) isomer. Therefore, the relative stability of one isomer over the other will be only ca. 1 kcal mol^{-1}.

(38) Rüchardt, C. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 830.

(39) Nicholas, A. M. d. P.; Arnold, D. R. *Can. J. Chem.* **1984**, *62*, 1850.

(40) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979–1985.

(41) Bordwell, F. G.; Cheng, J.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 1229–1231.

(42) Bordwell, F. G.; Zhang, X.; Cheng, J. P. *J. Org. Chem.* **1991**, *56*, 3216–3219.

On the other hand, Benson suggested that the RSE should be defined by comparison of the C–H bond with a C–H bond in a model compound that closely resembles the substituted compound of interest.[43] Had we chosen to base our calculations on cyclohexane (BDE = 96 kcal mol^{-1}), which is structurally closer to **1**, then the predicted RSE would be (96 – 90.8) + (96 – 89) = 12.2 kcal mol^{-1}, thus giving a calculated BDE for **1** of 83.8 kcal mol^{-1} which is 8.5 kcal mol^{-1} higher than the experimental value. Both definitions of RSE appear to be reasonable; however, it is clear that they lead to quite different conclusions concerning the additivity of the substitutent effects.

To understand these differences, it is useful to review the important assumptions that are implicit to the relative bond energy approach. The two key assumptions are the following: (1) the relative stabilites are additive and (2) the relative bond energies are a measure of the relative radical stabilities. It is clear from the two simple calculations above that in one case we arbitrarily define the stability of methyl to be 0.0 while in the other that of cyclohexyl to be 0.0. On an absolute scale, both cannot be correct, and since we know that cyclohexyl is stabilized relative to methyl, the former is probably closer to the truth. However, this does not imply that the summing of the putative RSE values, as if they were group enthalpy contributions, is justified.

The comparison of methyl to the radical derived from **1** (TM-3′), for example, is a combination of *at least* three contributions: (1) the conversion of methyl to a secondary radical, $\Delta H_{\mathrm{Me}\rightarrow\mathrm{RCHR}}$, (2) the conversion of a secondary radical to a substituted secondary radical, $\Delta H_{\mathrm{RCHR}\rightarrow\mathrm{XCHY}}$, and (3) the formation of a ring, $\Delta H_{\mathrm{XCHY}\rightarrow\mathrm{c\text{-}XCHY}}$. The general substituent, R, is not necessarily intended to represent an alkyl group (although we have chosen to do so in this case, see below). It is, rather, a hypothetical substituent that has the same intrinsic properties (i.e. radius, bond lengths and angles, electronegativity, etc.) as X or Y but does not interact electronically with the radical center through the π-system. The first of these enthalpy contributions is generally expected to be the largest and will vary depending on the nature of the substituent. The RSE can then be written as the sum of these three contributions (eq 7). The predicted RSE, RSE(TM-3′)$_{\mathrm{pred}}$, when the substituent effects are additive is given by eq 8. The comparisons of methyl to morpholin-2-yl (RSE(XCHR), eq 9) and δ-valerolacton-2-yl (RSE(YCHR), eq 10) have similar contributions; so, the addition of these RSE values, in fact, leads to an overestimate of the predicted BDE of **1** since two of the contributions have been counted twice (eq 11). This approach also has been used by Leroy who also defined the incremental stabilization effects of substituents (bond energy terms) relative to the alkyl analog.[44]

$$\mathrm{RSE(XCHY)} = \Delta H_{\mathrm{Me}\rightarrow\mathrm{RCHR}} + \Delta H_{\mathrm{RCHR}\rightarrow\mathrm{XCHY}} + \Delta H_{\mathrm{XCHY}\rightarrow\mathrm{c\text{-}XCHY}} \quad (7)$$

$$\mathrm{RSE(XCHY)_{pred}} = \Delta H_{\mathrm{Me}\rightarrow\mathrm{RCHR}} + \Delta H_{\mathrm{RCHR}\rightarrow\mathrm{XCHR}} + \Delta H_{\mathrm{RCHR}\rightarrow\mathrm{YCHR}} + \Delta H_{\mathrm{XCHY}\rightarrow\mathrm{c\text{-}XCHY}} \quad (8)$$

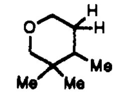
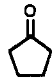
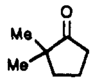
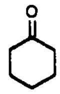
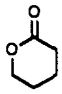
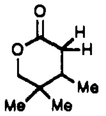
$$\mathrm{RSE(XCHR)} = \Delta H_{\mathrm{Me}\rightarrow\mathrm{RCHR}} + \Delta H_{\mathrm{RCHR}\rightarrow\mathrm{XCHR}} + \Delta H_{\mathrm{XCHR}\rightarrow\mathrm{c\text{-}XCHR}} \quad (9)$$

$$\underline{\mathrm{RSE(YCHR)} = \Delta H_{\mathrm{Me}\rightarrow\mathrm{RCHR}} + \Delta H_{\mathrm{RCHR}\rightarrow\mathrm{YCHR}} + \Delta H_{\mathrm{YCHR}\rightarrow\mathrm{c\text{-}YCHR}}} \quad (10)$$

$$\mathrm{RSE(XCH_2R)} + \mathrm{RSE(YCH_2R)} = 2\Delta H_{\mathrm{Me}\rightarrow\mathrm{RCHR}} + \Delta H_{\mathrm{RCHR}\rightarrow\mathrm{XCHR}} + \Delta H_{\mathrm{RCHR}\rightarrow\mathrm{XCHR}} + \Delta H_{\mathrm{XCHR}\rightarrow\mathrm{c\text{-}XCHR}} + \Delta H_{\mathrm{YCHR}\rightarrow\mathrm{c\text{-}YCHR}} \quad (11)$$

Therefore, we conclude that while the methane-based ΔBDE values may be close to the RSE's, *addition of these values is conceptually flawed* and violates the principles set out originally by Benson in his development of group additivities.[45] Although not explicit, this is certainly implied in Benson's original definition of radical stability which stipulated that comparisons should only be made between compounds with the same degree of substitution at the incipient radical center.[43,44] By starting with cyclohexane as the base compound, the sum of the RSE's will be closer to (but not precisely) the value predicted by eq 8 since they do not include terms such as $\Delta H_{\mathrm{Me}\rightarrow\mathrm{RCHR}}$ or $\Delta H_{\mathrm{XCHY}\rightarrow\mathrm{c\text{-}XCHY}}$.

Table II. Calculated (MM2) Bond Dissociation Enthalpies (BDE) and Strain Energy Changes (ΔSE) for the C–H Homolysis of Some Hydrocarbons

R–H	BDE (kcal mol^{-1}) MM2	BDE (kcal mol^{-1}) lit.	ΔSE (kcal mol^{-1})[a]
CH_3CH_2—H	99.6	100.1[b]	0.8
$(CH_3)_2CH$—H	97.0	96.3[b]	0.8
c-C_5H_{10}	95.8	96[b]	–0.4
c-C_6H_{12}	97.9	96[b]	1.7
	96.7		0.5
$CH_3C(O)CH_2$—H	88.7	94[c]	–1.3
$CH_3C(O)CH(Me)$—H	86.5		–0.6
	83.7	88[c]	–3.6
	82.7	89[c]	–4.6
	83.9	88[d]	–3.3
EtOC(O)CH_2—H	88.7		–1.2
EtOC(O)CH(Me)—H	87.0		–0.1
	83.4		–3.9
	83.5		–3.7

[a] Change in the overall strain energy for the following reaction: R–H → R• + H•. ΔSE = SE(R•) – SE(R–H). [b] Griller, D.; Kanabus-Kaminska, J. M.; Maccol, A. *J. Mol. Struct.* (*Theochem*) **1988**, *163*, 125–131. [c] Reference 15. [d] Bordwell, F. G.; Harrelson, J. A., Jr. *Can. J. Chem.* **1990**, *68*, 1714.

The difficulty in defining a precise captodative stabilization energy also is apparent from the second assumption that the relative bond energies are a measure of the relative radical stabilities. Separating the steric and electronic effects on the ground state of a hydrocarbon from those on the radical clearly is not straightforward (see above). We have used MM-2 force field calculations in order to gain some insight into the role of strain on relative bond energies, especially in relation to the differences between the acyclic and cyclic systems that we have studied. Data for a number of hydrocarbons, ketones, and esters are given in Table II along with literature values where available. In addition, the calculated strain energy change, ΔSE, associated with the homolysis of the C–H bond is included. In this table, positive ΔSE values imply that the radical is more strained than the hydrocarbon and negative ΔSE values imply the reverse. For the hydrocarbons and the acyclic ketones and esters, the removal of a hydrogen atom has little effect on the total strain. However, removal of a hydrogen atom from all of the cyclic ketones and lactones results in a significant relief of strain (ca. 4 kcal mol^{-1}) in the radical compared to the starting carbonyl. This is probably related to the radical being more flexible;[46,47] i.e. gauche and 1,3

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(44) Leroy, G.; Peeters, D.; Sana, M.; Wilante, C. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merényi, R., Eds.; Reidel: Dordrecht, 1986; Vol. 189, pp 1–48.

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interactions can be minimized. The increase in strain in cyclohexyl and the decrese in strain in cyclopentyl are consistent with this reasoning.

The calculated relative bond energy of cyclopentanone compared to acetone (6 kcal mol^{-1}) is similar to that reported by Bordwell (Table II).[13] The implication of the force field calculations is that 2–3 kcal mol^{-1} of this difference may be attributed to destabilization of the ketone with the remainder (3–4 kcal mol^{-1}) assigned to the RSE. It should be emphasized that the bond energies are the fundamentally important thermodynamic data. The question of whether a hydrocarbon is destablized or a radical is stabilized (or both), however, presents obvious limitations on our ability to understand, quantitatively, substituent effects on the radicals themselves. Unfortunately, the unavailability of force field parameters precludes direct calculations of **1**–**8**. However, by analogy to the lactones, the change in the strain energy in the hydrocarbon compared to the radical provides a reasonable explanation for the difference between the measured bond energies of **5** and **7** versus **1** and **2**.

Conclusions

Carbon–hydrogen bond dissociation energies and absolute rate constants for hydrogen atom abstraction by the *tert*-butoxyl radical have been measured for a number of aliphatic amines, including two captodatively substituted compounds (**1** and **2**). The bond energies, determined by photoacoustic calorimetry, cover a range of about 15 kcal mol^{-1} (ca. 90 kcal mol^{-1} for the aliphatic amines to 75 kcal mol^{-1} for **1**). The C–H bonds of **1**–**4** with the *tert*-butoxyl radical are far more reactive than simple cyclic and acyclic amines. These reactions illustrate the importance of the stereoelectronic effect: in this case, conjugation between the incipient radical center and the developing π-system. In addition, there is evidence suggesting that relief of ring strain also plays an important role in determining both the BDE and the reactivity of the amine.

The estimation of the captodative stabilization energies of **1** and **2** from the BDE data is difficult for a number of reasons outlined above and illustrates the importance of the caution given by Sustmann and Korth in their recent review.[11] The usual assumption that relative BDE(C–H) values are a measure of relative radical stabilization energies (RSE) is not justified when homolysis can lead to relief of ring strain. For lactones, evidence suggests that strain effects on the hydrocarbon versus those on the radical may have a significant effect. In addition, we have shown that the addition of RSE's from a methane-based scale will overestimate the combined effect of two substituents on a C–H bond. We conclude that the method proposed originally by Benson[43] provides a better estimate.

Finally, keeping in mind the attendant uncertainties, it is worthwhile to attempt to estimate the "captodative stabilization energy" in the radical TM-3′. We believe that the best approximation of group enthalpy contributions will come from comparisons of cyclohexane, δ-valerolactone, and morpholine, i.e. the Benson approach. In this case, using BDE's from Tables I and II, the estimated bond energy of **1** is ca. 84 kcal mol^{-1} which is 8.5 ± 4 kcal mol^{-1} higher than the measured value. Therefore, *we conclude that the substituent effects on the BDE's are not additive, and for* **1** *they appear to be synergetic by ca. 9 kcal mol^{-1}.* This should not be interpreted as a measure of the captodative effect on the radical; it is a measure of the combined effects on the hydrocarbon and on the radical. However, if strain energy differences account for ca. 3–4 kcal mol^{-1} of this difference, there is about 5–6 kcal mol^{-1} remaining. Given experimental error on the sum of the ΔBDE's of ±4 kcal mol^{-1} we conclude that the difference, while small, is significant. For the acyclic analog, **5**, using propane, ethyl propionate (BDE = 92 kcal mol^{-1}), and triethylamine (BDE = 89 kcal mol^{-1} [48]) the estimated BDE is 84 kcal mol^{-1}. Here strain energy differences are expected to be less important (i.e. $\Delta\text{BDE} \approx \text{RSE}$) and the difference between the estimated and the measured value is between 1 ± 4 and 5 ± 4 kcal mol^{-1} (using the upper and lower limits from Table I).

Experimental Section

General Remarks. Infrared spectra were obtained with a Perkin-Elmer Model 1600 FTIR spectrometer, UV–vis spectra were obtained with a Hewlett-Packard Model 8452 spectrometer, and mass spectra were obtained with a VG Instruments 7070 EQ-HF spectrometer. NMR spectra were obtained with a Varian VXR 300 MHz spectrometer, and chemical shifts are reported in ppm on the δ scale from internal tetramethylsilane or respective solvent signal. EPR spectroscopy was performed with a Varian 109E spectrometer. Gas chromatography was performed with a Varian Aerograph Model 1700 chromatograph equipped with a thermal conductivity detector, and flash chromatography was performed as described by Still and co-workers.[49] Microanalyses were performed by Atlantic Microlab, Norcross, GA. *N,N*-Dimethylglycine, ethyl ester (**5**) was purchased from Adrich and distilled prior to use. Gycine hydrochloride, *tert*-butyl ester was purchased from Adrich. The free base was generated by reaction with aqueous NaOH, extracted into diethyl ether, and purified by distillation. Other chemical reagents were obtained from Aldrich Chemical Co. (Milwaukee, WI).

4,5,5-Trimethyl-2-oxomorpholine (1). 4,5,5-Trimethyl-2-oxomorpholine (**1**) was prepared as described by Benson et al.[7] and further purified by preparative GLC on a 6.4 mm by 2.1 m column of 5% SE-30 on 60/80 mesh high performance Chromosorb W. The column was eluted at 65 °C with helium at 60 mL/min. A 0.5 M solution of purified **1** had an optical density at 337 nm of 0.02.

3,5,5-Trimethyl-2-oxomorpholine (2). 5,6-Dihydro-3,5,5-trimethyl-1,4-oxazin-2-one was prepared from reaction of ethyl pyruvate with 2-amino-2-methylpropanol as described by Koch and co-workers.[50] 5,6-Dihydro-3,5,5-trimethyl-1,3-oxazin-2-one (2.5 g, 0.018 mol) in 10 mL of ethyl acetate was added to a mixture of 0.1 g of 10% palladium on carbon catalyst suspended in 10 mL of ethyl acetate. The mixture was reacted with 1 atm of hydrogen at ambient temperature over a period of 12 h. The catalyst was removed by suction filtration through Celite, and the solvent was removed by rotary evaporation. An ^{1}H NMR spectrum of the crude product in $CDCl_3$ showed clean formation of **2** in comparison with the spectrum of **2** obtained from disproportionation of 3,5,5-trimethyl-2-oxomorpholin-3-yl (TM-3).[51] The material was further purified by three successive silica gel flash chromatographies eluting with ethyl acetate. A 0.5 M solution of purified **2** in benzene had an optical density at 337 nm of 0.055.

Methyl Bromomethoxyacetate. Methyl bromomethoxyacetate was prepared by using a modification of the procedure reported by Atkinson et al.[52] A solution of 25.0 g (0.24 mol) of methyl methoxyacetate in 50 mL of carbon tetrachloride was added to a suspension of 42.8 g (0.24 mol) of *N*-bromosuccinimide in 150 mL of carbon tetrachloride. The reaction mixture was heated at reflux with stirring for 20 h and then filtered. The solvent of the filtrate was removed by rotary evaporation. Pure methyl bromomethoxyacetate was collected as a colorless liquid (40.0 g, 91%) by vacuum distillation at 44 °C at 0.5 Torr. The distilled material had the following ^{1}H NMR spectrum ($CDCl_3$): δ 3.55 (s, 3 H), 3.82 (s, 3 H), 5.96 (s, 1 H).

2-Carbomethoxy-3-ethyl-4,4-dimethyl-1,3-oxazolidine (3). 2-(Ethylamino)-2-methylpropanol was prepared as described by Benson and coworkers.[7] A solution of 3.83 g (0.0327 mol) of 2-(ethylamino)-2-methylpropanol in 50 mL of benzene was placed in a two-neck round-bottom flask. One of the necks was mounted with a Dean-Stark trap containing 4A molecular sieves. The second neck was mounted with an addition funnel containing a solution of 3.00 g (0.0164 mol) of methyl bromomethoxyacetate in 20 mL of benzene. The addition funnel did not have a pressure equalizing side arm; consequently, distillation of methanol formed during the course of the reaction into the addition funnel was prevented. An earlier experiment showed that methanol reacted with methyl bromomethoxyacetate to form methyl dimethoxyacetate. Methyl bromoacetate was added dropwise while the reaction mixture was heated at reflux with stirring. After the addition, heating at reflux was continued for 8 h. The reaction mixture was filtered and the solvent was removed from the filtrate by rotary evaporation. Pure product was collected as a colorless liquid (3.35 g, 70%) by vacuum distillation at 60–65 °C at 0.1 Torr. The purified material showed the following properties: ^{1}H NMR ($CDCl_3$) δ 1.05 (t, X of ABX_3 pattern, $J_{AX} = J_{BX} = 7$ Hz, 3 H), δ 1.09 (s, 3 H), 1.18 (s, 3 H), 2.54 (A of ABX_3, $J_{AB} = 12$ Hz, $J_{AX} = 7$ Hz, 1 H), 2.76 (B of ABX_3, $J_{AB} = 12$ Hz, $J_{BX} = 7$ Hz,

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1 H), 3.72 (d, $J = 7$ Hz, 1 H), 3.76 (s, 3 H), 3.88 (d, $J = 7$ Hz, 1 H), 4.58 (s, 1 H); IR (thin film) 2985, 2882, 1783, 1767, 1466, 1437, 1393, 1366, 1200, 1100 cm^{-1}; mass spectrum (CI$^+$, isobutane) m/z (relative intensity) 188 (M + 1, 50), 128 (100), 116 (20), 74 (10). Anal. Calcd for $C_9H_{17}NO_3$: C, 57.74; H, 9.15; N, 7.48. Found: C, 57.49; H, 9.18; N, 7.33. A 0.5 M solution of **3** in benzene had an optical density at 337 nm of less than 0.02.

3-Ethyl-2,4,4-trimethyl-1,3-oxazolidine (4). 2-(Ethylamino)-2-methylpropanol was prepared as described by Benson and co-workers.[7] Acetaldehyde (13.83 g, 0.314 mol) was added to a round-bottom flask containing 9.20 g (0.0786 mol) of 2-(ethylamino)-2-methylpropanol in 200 mL of benzene at ambient temperature. The flask was equipped with a Dean-Stark head, and the reaction mixture was heated at reflux with stirring until no additional water was collected. Pure **4** was obtained as a colorless liquid (9.33 g, 83%) by vacuum distillation at 55 °C at 8 Torr. The product was characterized from the following data: ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 3 H), 1.04 (t, X of ABX_3 pattern, $J_{AX} = J_{BX} = 7$ Hz, 3 H), 1.09 (s, 3 H), 1.23 (d, $J = 5$ Hz, 3 H), 2.28 (A of ABX_3, $J_{AB} = 13$, $J_{AX} = 7$ Hz, 1 H), 2.59 (B of ABX_3, $J_{AB} = 13$ Hz, $J_{BX} = 7$ Hz, 1 H), 3.52 (d, $J = 7$ Hz, 1 H), 3.58 (d, $J = 7$ Hz, 1 H), 4.26 (q, $J = 5$ Hz, 2 H); IR (thin film) 2974, 2594, 1464, 1393, 1302, 1026, 976, 934, 862, 834, 740, 649 cm^{-1}; mass spectrum (EI$^+$) m/z (relative intensity) 143 (3), 142 (4), 129 (5), 128 (49), 114 (12), 100 (19), 86 (100), 84 (20), 74 (14), 58 (42), 42 (27); high resolution M$^+$, m/z 143.1299; calcd for $C_8H_{17}NO$, m/z 143.1310. A 0.5 M solution of the purified **4** had an optical density at 337 nm of less than 0.02.

Bi(2-carbomethoxy-3-ethyl-4,4-dimethyl-1,3-oxazolidin-2-yl). A 20 mm o.d. × 200 mm quartz tube was charged with 2.1 g (11 mmol) of 3-ethyl-4,4-dimethyl-2-carbomethoxyoxazolidine (**3**), 0.82 g (5.6 mmol) of di-*tert*-butyl peroxide, and 65 mL of spectral grade benzene and equipped with a reflux condenser. The solution was oxygen degassed with prepurified argon for 10 min and irradiated with continuous degassing for 24 h in a Rayonet Photochemical Reactor (Model RPR 100, Southern New England Ultraviolet Co., Hamden, CT) equipped with sixteen 3000-Å lamps. The solvent was removed by rotary evaporation and the residue was purified by flash chromatography with use of a 30 mm o.d. flash column eluting with 20% ethyl acetate/hexanes (v/v). The desired fractions were combined and the solvent rotary evaporated. After air drying 0.60 g (29%) of bi(2-carbomethoxy-3-ethyl-4,4-dimethyl-1,3-oxazolidin-2-yl) was collected as a mixture of meso and *dl* isomers. The ^{1}H NMR spectrum in $CDCl_3$ showed both stereoisomers: (major isomer, 75%) δ 1.16 (t, X of ABX_3 pattern, $J_{AX} = J_{BX} = 7$ Hz, 6 H), 1.28 (s, 6 H), 1.35 (s, 6 H), 2.64 (A of ABX_3, $J_{AB} = 12$ Hz, $J_{BX} = 7$ Hz, 2 H), 3.12 (B of ABX_3, $J_{AB} = 12$ Hz, $J_{BX} = 7$ Hz, 2 H), 3.72 (d, $J =$ J Hz, 1 H), 3.70 (s, 6 H), 3.94 (d, $J = 7$ Hz, 2 H), 4.14 (s, 2 H); (minor isomer, 25%) δ 1.05 (t, X of ABX_3, $J_{AX} = J_{BX} = 7$ Hz, 6 H), 3.70, (s, 6 H), the other peaks overlapped with the major isomer; mass spectrum (CI$^+$, isobutane) m/z (relative intensity) 285 (M + 1, 35), 185 (10), 142 (100). Anal. Calcd for $C_{18}H_{32}N_2O_6$: C, 58.05; H, 8.66; N, 7.52. Found: C, 57.92; H, 8.70; N, 7.53.

Attempts To Form 2-Carbomethoxy-3-ethyl-4,4-dimethyl-1,3-oxazolidin-2-yl from Bi(2-carbomethoxy-3-ethyl-4,4-dimethyl-1,3-oxazolidin-2-yl). Bi(2-carbomethoxy-3-ethyl-4,4-dimethyl-1,3-oxazolidin-2-yl) (5 mg) was dissolved in 2 mL of a 1 M solution of silver nitrate in methanol. No metallic silver was formed even upon heating a solution to 100 °C. No EPR signal was observed upon heating an ethanol solution of bi(2-carbomethoxy-3-ethyl-4,4-dimethyl-1,3-oxazolidin-2-yl) to 70 °C in the cavity of an EPR spectrometer.

Photoacoustic Calorimetry. The photoacoustic apparatus has been described in detail elsewhere.[20-22] Solutions were photolyzed by a Molectron UV24 pulsed nitrogen laser (337.1 nm, 10 ns pulse width) and the resulting shock waves were detected by a Panametrics V101 transducer (2 μs response), amplified by a Panametrics Model 5670 ultrasonic preamplifier and signal averaged with a Tektronix Model 7D20 digital oscilloscope. Optical densities were measured with a Hewlett-Packard Model 8450 diode array spectrometer. In all cases, the slope from a plot of the normalized photoacoustic signal versus ($1-10^{-OD}$), where OD is the optical density of the solution at 337 nm, was linear with a correlation coefficient >0.999. The observed fraction of heat deposited in solution, α_{obs}, was the ratio of the slope of this line for reaction 3 versus that for *o*-hydroxybenzophenone.

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The Temperature and Medium Dependencies of *cis*-Stilbene Fluorescence. The Energetics for Twisting in the Lowest Excited Singlet State

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Abstract: Fluorescence quantum yields of *cis*-stilbene-d_0 and -d_2 were measured as a function of temperature in *n*-hexane and *n*-tetradecane. *cis*-Stilbene fluorescence quantum yields were decomposed into emission contributions from ${}^1c^*,\phi_{fc}{}^c$, and adiabatically formed ${}^1t^*,\phi_{ft}{}^c$, by application of principal-component analysis. Rate constants, k_{cp} for the ${}^1c^* \rightarrow {}^1p^*$ torsional process, calculated from $\phi_{fc}{}^c$ give Arrhenius activation parameters $E_{cp}{}^a = 0.33 \pm 0.08$ and 1.90 ± 0.08 kcal/mol and $\ln A = 27.80 \pm 0.13$ and 30.09 ± 0.12 for *n*-hexane (*c*-d_0 and *c*-d_2) and *n*-tetradecane (*c*-d_0), respectively. Deuteration of the olefinic positions has no effect on k_{cp} in *n*-hexane, but diminishes k_{cp} by ~10% in *n*-tetradecane. Applying the medium-enhanced barrier model on these k_{cp}'s and on literature k_{cp}'s in methylcyclohexane/methylcyclopentane gives $E_{cp}{}^a = -(1.07 \pm 0.05) + (0.89 \pm 0.01)E_{\eta_s}$ kcal/mol indicating a negative intrinsic barrier, $E_c{}^0 = -1.07 \pm 0.05$ kcal/mol, and a nearly full imposition of the activation energy for viscous flow, E_{η_s}, to the ${}^1c^* \rightarrow {}^1p^*$ process, independent of deuterium substitution at the olefinic positions. The $\phi_{ft}{}^c$ values are remarkably T independent in both solvents. Assuming that adiabatic formation of ${}^1t^*$ takes the ${}^1c^* \rightarrow {}^1p^* \rightarrow {}^1t^*$ pathway, these results indicate that ${}^1p^*$ and ${}^1t^*$ represent essentially isoenergetic regions in the potential energy surface of the lowest excited stilbene singlet state, thus providing the first experimental estimate of the energy of the perpendicular singlet state, ${}^1p^*$.

The effect of medium friction on the rates of very fast unimolecular reactions has been the topic of many recent experimental and theoretical investigations.[1] The trans ⇄ cis photoisomerization of stilbene is at the center of much of this work because

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