4.13 (t, J = 2.9 Hz, 1 H), 8.2 (d, J = 9.0 Hz, 2 H), 8.33 (d, J = 9.0, 2 H). ^{13}C NMR ($CDCl_3$) data of **26a**: δ 206.9 (m), 204.7 (qi, $^3J_{C,H}$ = 6.0 Hz), 163.2 (s), 151.0 (t, $^3J_{C,H}$ = 7.3 Hz), 134.3 (t, $^3J_{C,H}$ = 6.1 Hz), 131.0 (dd, $^1J_{C,H}$ = 169.0 Hz, $^3J_{C,H}$ = 5.5 Hz), 123.8 (dd, $^1J_{C,H}$ = 170.9 Hz, $^3J_{C,H}$ = 3.7 Hz), 82.9 (s), 82.0 (d, $^1J_{C,H}$ = 150.1 Hz), 57.3 (qd, $^1J_{C,H}$ = 142.8 Hz, $^3J_{C,H}$ = 4.3 Hz), 40.7 (br t, $^1J_{C,H}$ = 129.4 Hz), 36.3 (t, $^1J_{C,H}$ = 130.6 Hz), 27.6 (q, $^1J_{C,H}$ = 128.6 Hz), 26.0 (t, $^1J_{C,H}$ = 133.7 Hz). Further signals attributed to isomer **26b**: 205.9, 204.0, 33.8. MS (CI, NH_3): 353 ($M^+ + NH_4^+$, 45), 306 (9), 188 (100), 171 (11), 156 (19). Anal. Calcd for $C_{16}H_{17}NO_7$: C, 57.31; H, 5.11. Found: C, 57.05; H, 5.44.

[1*R,2*R**]-1-Acetyl-1,2-dihydroxycyclohex-3-ene (24a) and [1*R**,2*S**]-1-Acetyl-1,2-dihydroxycyclohex-3-ene (24b).** To a solution of **18a**/**18b** (>95:<5) (2.3 g, 6.6 mmol) in anhydrous CH_2Cl_2 (5 mL) was added MeOH (1 mL) and anhydrous K_2CO_3 (0.5 g). After being stirred at room temperature for 10 min, the mixture was diluted with CH_2Cl_2 (10 mL) and washed with brine (3 × 5 mL). The organic layer was dried (Na_2SO_4) and the solvent was evaporated in vacuo. The residue was divided in two parts, the first one (1.2 g) was purified by column chromatography on Florisil (14 g, petroleum ether/EtOAc, 85:15), yielding 0.49 g (95%) of **24a**/**24b** (>95:<5) as a light-yellow oil. The second part (1.2 g) was purified on Florisil/10% K_2CO_3 (16 g, petroleum ether/EtOAc, 9:1), providing 0.5 g (97%) of a mixture of **24a**/**24b** (40:60). This mixture was separated by medium pressure chromatography (petroleum ether/EtOAc, 85:15), yielding 0.19 g of **24a** as colorless crystals and 0.29 g of **24b** as a colorless oil.

24a: R_f 0.34 (1/1 ethyl acetate–hexane); mp 60–61 °C; IR (film) 3400, 3010, 2900, 1685, 1350, 1200, 1120 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.7–2.7 (m, 6 H, 2 CH_2, 2 OH), 2.35 (s, 3 H, CH_3CO), 4.1 (br s, 1 H, C-2), 5.95 (m, 2 H, H-3, H-4); MS (70 eV) 156 (M^+, 0.2), 138 ($M^+ - H_2O$, 0.3), 95 (8), 85 (29), 43 (36), 40 (100). Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.56; H, 7.79.

24b: R_f 0.4 (1/1 ethyl acetate–hexane); IR (film) 3400, 3010, 2900, 1690, 1370, 1250 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.5–2.4 (m, 5 H, 2 CH_2, OH), 2.35 (s, 3 H, CH_3CO), 4.0 (br s, 1 H, OH), 4.6 (br s, 1 H, C-2), 5.68 (dm, J = 10.0 Hz, H-3), 5.98 (dm, J = 10.0 Hz, H-4); MS (70 eV) 156 (M^+, 3), 113 (55), 96 (17), 95 (100), 87 (12), 70 (41), 67 (89). Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 61.64; H, 7.86.

[1*R,2*S**]-1-Acetyl-1,2-(isopropylidenedioxy)-3-cyclohexene (25b).** To a solution of a mixture of **24a**/**24b** (4:6) (0.35 g, 2.2 mmol), *p*-TsOH (0.15 g, 0.87 mmol), and anhydrous DMF (0.6 mL) in dry CH_2Cl_2 (2 mL) at 0 °C was slowly added 2,2-dimethoxypropane (0.58 g, 5.6 mmol). After being stirred at this temperature for 19 h, the mixture was diluted with CH_2Cl_2 (20 mL) and washed with aqueous 5% NH_4OH (2 × 2 mL) and brine (2 × 3 mL). The aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were dried (Na_2SO_4) and the solvent was removed in vacuo. The obtained oil was purified by column chromatography on Florisil/10% K_2CO_3 (30 g, petroleum ether/EtOAc, 7:3) and afforded 0.26 g (98%) of **25b** as a colorless oil and 0.13 g (93%) of unreacted **24a**.

25b: R_f 0.6 (1/4 ethyl acetate–hexane); IR (film) 3020, 2940, 1700, 1390, 1260, 1240, 1120, 1080 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.4 (s, 3 H), 1.5 (s, 3 H), 1.8 (m, 2 H), 2.1 (m, 2 H), 2.36 (s, 3 H, CH_3CO), 4.86 (m, 1 H, H-2), 6.1 (m, 2 H); MS (70 eV) 181 ($M^+ - CH_3$, 1), 153 (38), 138 (1), 123 (3), 96 (20), 95 (100), 67 (31). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.57; H, 8.16.

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Supplementary Material Available: Table of MINDO/3 calculations of energies and coefficients of the FMOs for dienophiles **1** and MVK (1 page). Ordering information is given on any current masthead page.

AM1 Calculations of Substituent Effects in Retro-Diels–Alder Reactions

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The AM1 method has been used for investigating the effects of substituents on retro-Diels–Alder reactions, and the results have been compared with experimental data. Transition structures for butadiene reacting with ethylene and acrolein are quite close to those obtained with ab initio methods. The calculated asynchonicity of the retro-Diels–Alder reaction of substituted bicyclo[2.2.2]octa-2,5-dienes and ethanoanthracenes depends on substituents, with electron-donating groups making the TS more asymmetrically. The calculated activation energies for these reactions are too high compared to experimental data, but trends in relative activation energies for different substituents are reproduced reasonably well, although there are exceptions. Calculated activation entropies for unsubstituted systems are in good agreement with ab initio values and experimental data, but the variation of activation entropy with substituents is not reproduced.

Introduction

The Diels–Alder (DA) reaction continues to be one of the more popular reactions in organic synthesis due to the control of stereochemistry it provides,[1] and the reverse reaction has been used for protecting a diene moiety during synthetic sequences.[2] The qualitative effects of different functional groups on the reaction rate are well known,[3] electron donors on the diene and electron acceptors on the dieneophile accelerate the reaction,[4] and these effects can be rationalized by FMO theory.[6] Despite the large number of DA reactions known, very few systematic studies of the effects of different functional groups have appeared, but

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(4) Inverse electron demand DA reactions are also known, but they presumably occur via reaction mechanisms involving polar intermediates, see e.g. ref 3 and 5.

(5) Gompper, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 312.

(6) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*. Wiley: London, 1976.

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recently Czarnik et al. have published data on the retro-DA reaction of substituted ethanoanthracene compunds.[7]

The mechanism of the DA reaction has been the subject of much dispute in the literature, the discussion being centered around the question of whether the reaction is concerted or nonconcerted, and whether a concerted reaction is synchronous or not.[3,8–11] For the textbook example of butadiene reacting with ethylene to give cyclohexene, both experimental[8] and ab initio calculations[8–10] agree that the reaction is concerted and synchronous. Earlier semiempirical calculations using the MINDO/3[12] and MNDO[13] methods gave results that were interpretated in terms of a nonconcerted reaction occurring via a biradical intermediate,[11,14] but the recently introduced AM1 method[15] now concures with ab initio results.[8–11,16] For unsymmetrical systems the widespread opinion is that the DA reaction is concerted (but asynchonous), unless the two components have very different polarity in which case zwitterionic intermediates may be formed,[5,17] or are polyhalogenated with which case biradical intermediates prevail.[18]

While there is little doubt that high level ab initio methods can calculate absolute activation energies with an accuracy of a few kcal/mol,[19] they are limited to small (model) systems of the reaction of interest, while semiempirical methods can be applied to systems much closer to the experimental ones. The main advantage of semiempirical over ab initio calculations is that they require much less computer time, but in contrast to ab initio methods they are unable to provide an internal check on the accuracy of the calculated results. Ab initio methods can, at least in principle, be successively improved with respect to basis set and electron correlation to provide a measure of the reliability of the methods used, but the performance of semiempirical methods can only be evaluated by comparisons between calculated values and experimental data. While semiempirical methods are quite successful in calculating properties of ground-state molecules (not surprisingly since they are parameterized to do so), much less is known about their ability to describe transition structures (i.e. calculate activation parameters). It is often implicitly assumed that the same degree of accuracy holds for transition states as for ground states, and calculated results for transition states have been used to draw conclusions regarding reaction mechanisms.[11,14,20] While this assumption may be true for some reaction types, it is clearly of interest to compare calculated values with experimental data for as many reactions as possible. We here report AM1 calculations for the retro-Diels–Alder reaction of some substituted ethanoanthracenes for which good experimental data are available, and especially concentrate on whether the AM1 method is capable of accurately predicting substituent effects.

Computational Methods

The AM1 method[15] is an improved version of the MNDO method[13] which is based on a single determinant wave function using a minimal valence basis set and invoking the NDDO approximation. The wave function can either be of a spin-restricted type (orbitals are either doubly occupied or empty) or a spin-unrestricted type (all electrons are allowed to have seperate orbitals). For typical ground-state singlet molecules an unrestricted wave function is identical to a restricted one, i.e. doubly occupancy of the orbitals is the most favorable electron configuration. For transition structures (TS) where bonds are stretched, unrestricted wave functions often give lower energies than restricted ones, but this is not necessarily a desireable feature since the energy lowering is a result of mixing higher spin states with the singlet state. Unrestricted "singlet" wave functions for transition structures are typically very heavily contaminated by higher spin states (i.e. $\langle S^2 \rangle = 0.7–1.4$),[11] and this generally leads to distorted potential energy surfaces with false minima and unrealistic energies.[21] For the parent DA reaction of ethylene and butadiene ab initio RHF[8,10b] and MCSCF,[9] and spin-restricted semiempirical methods (MINDO/3, MNDO, AM1)[11,14] all agree that the reaction is concerted, although the MINDO/3 and MNDO transition structures are extremely asynchronous (i.e. being "biradicaloid" in character).[16] UHF methods, either ab initio[8] or semiempirical, and semiempirical methods including CI[11,14] all predict that the reaction is nonconcerted, occurring via a biradical intermediate. One must recognize, however, that the use of CI with semiempirical methods makes calculated heats of formation too low since electron correlation is included twice, once implicitly via the parameters and once explicitly during the CI procedure. Experimental data[8] are only consistent with a concerted reaction, but they are unable to distinguish between a synchronous and an as-

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(16) Very recently Stewart has published a new set of rigorously optimized parameters for use with the MNDO method, and labeled this MNDO-PM3 (Stewart, J. J. P. *J. Comp. Chem.* **1989**, *10*, 209, 211). Preliminary results with the MNDO-PM3 method shows that the parent DA reaction of butadiene and ethylene is calculated to be synchronous, thus concuring with AM1 results but disagreeing with the original MNDO method. For the different TS's of butadiene reacting with acrolein, the TS geometries are similar to those obtained with the AM1 method, but they are significantly less asymmetrical (ΔR_{ts} for A, B, C, D are 0.114, 0.094, 0.110, 0.084 Å, respectively, i.e. the AM1 results are closer to the ab initio ones). Relative energies of the four TS's are: A:B:C:D = 0.0:–0.3:0.8:–0.1 kcal/mol, i.e. different from the AM1 results but not in any better agreement with the HF/6-31G* values, although the favored TS now has the endo configuration. Also the bicyclo ester reaction (1b, R_2 = H) is calculated to be less asymmetrically than with AM1. The fact that a better method for optimizing the atomic parameters that determine the MNDO method is capable of changing the parent DA reaction from being very asymmetrically to completely synchronous shows that one should be extremely careful in drawing conclusions regarding reaction mechanisms from semiempirical calculations. Notice also that Stewart's results suggest that some of the parameters in MNDO-PM3 (and presumably also AM1) are not very well defined from the experimental data, as evident from several very small eigenvalues in the error Hessian matrix.

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Table I. Calculated Bond Distances for Different TS's in the Reaction of Butadiene and Acrolein[a]

	A		B		C		D	
method	$\bar{R}_{ts}$	ΔR_{ts}	$\bar{R}_{ts}$	ΔR_{ts}	$\bar{R}_{ts}$	ΔR_{ts}	$\bar{R}_{ts}$	ΔR_{ts}
HF/STO-3G[b]	2.228	0.200	2.225	0.160	2.229	0.194	2.227	0.158
HF/3-21G[b]	2.221	0.265	2.211	0.155				
AM1	2.129	0.188	2.132	0.160	2.131	0.183	2.131	0.144

[a] $\bar{R}_{ts}$ and ΔR_{ts} in angstroms, the TS configurations are as follows: A, endo,s-cis; B, endo,s-trans; C, exo,s-cis; D, exo,s-trans. [b] Reference 28.

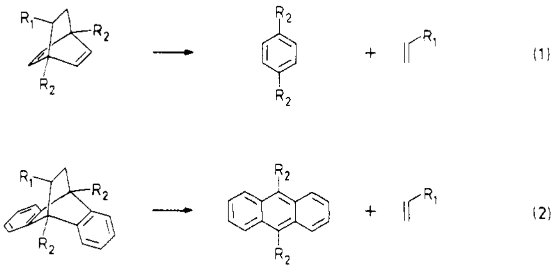
ynchronous reaction. The existence of biradical intermediates when using UHF or semiempirical CI methods is almost certainly an artifact of the spin contamination problem or the double inclusion of electron correlation for CI methods.

The ab initio MCSCF study of Bernardi et al.[9] found two transition structures for the concerted reaction of butadiene and ethylene, one corresponding to a synchronous reaction, and one corresponding to a "two-stage" reaction[22] with forming bond lengths of 1.96 and 3.46 Å. While the wave function for the former can be reasonably well described by an RHF wave function, the latter requires MCSCF-based methods. The relative energies of the two TS's were calculated with two different MCSCF wave functions, CAS1 (four electrons in four orbitals) and CAS2 (six electrons in six orbitals), employing the STO-3G and 4-31G basis sets. With the STO-3G basis the "two-stage" TS is favored by 8.4 and 2.1 kcal/mol at the CAS1 and CAS2 level, respectively, while the synchronous TS is lowest in energy (by 1.5 kcal/mol) at the CAS1/4-31G level. Although these calculations are quite impressive by today's standards, they are still far from the level necessary for providing an accurate estimate of the energy difference between the two TS's, which would require much better basis sets and inclusion of dynamic electron correlation. The results, however, do indicate that both better basis sets and better wave functions preferentially favor the synchronous pathway. Semiempirical methods are at present limited to single determinant based wave functions, and our results are consequently only valid for systems reacting via a synchronous type pathway. Whether the systems considered here pass that criteria is unknown, and that should be kept in mind when reading the conclusions presented below.

All geometries, both ground (GS) and transition structures, have been completely optimized using an implementation in the AMPAC program[23] of the method described by Baker.[24] For systems with conformational degrees of freedom (e.g. rotation of the ester group in reactions labeled b) several different structures are possible, but only results for the lowest energy conformation in each case are reported. For several of the systems the nature of the GS and TS was confirmed by the presence of 0 and 1, respectively, negative eigenvalues in the second derivative matrix. Entropies and enthalpic correction factors (zero point energy and finite temperature contributions) have been evaluated by standard formulas[25] based on calculated harmonic vibrational frequencies.

Results and Discussion

In addition to the anthracene systems studied by Czarnik et al. (reactions 2b and 2c),[7] we have also performed calculations on the smaller bicyclo[2.2.2]octa-2,5-diene system (reactions labeled 1) since it computationally is much simpler. As shown below the calculated substituent effects are very similar for the two systems, although absolute activation energies differ significantly. In the following we will use the nomenclature for the anthracene system when discussing substituent effects, i.e. refer to systems labeled b as 9,10-disubstituted even though for the bicyclo systems they are 1,4-disubstituted.



a : $R_1 = H$, R_2 = Variable
b : $R_1 = CO_2CH_3$, R_2 = Variable
c : $R_2 = H$, R_1 = Variable

We will start our evaluation of the AM1 method by comparing calculated results with relevant ab initio results and experimental data for the two parent reactions 1a and 2a (R_2 = H). Calculated geometries of ground and transition structures are in general rather unremarkable and will not be discussed in any detail. The only parameter warranting some discussion is the (average) length of the breaking C–C bond(s) at the TS, denoted in the following by $\bar{R}_{ts}$, and the asymmetry of the TS defined as the difference between the two bond lengths, denoted by ΔR_{ts}. In all cases the longer of the two bonds is associated with the most substituted carbons.

The AM1 calculated TS of the DA reaction between ethylene and butadiene shows that the reaction is concerted and synchronous, in agreement with ab initio calculations. The $\bar{R}_{ts}$ distance of 2.119 Å is slightly shorter than ab initio values of 2.210 Å (HF/3-21G[8]) and 2.244 Å (MCSCF/4-31G[9]), but in general the structures are all very similar. The AM1 calculated $\Delta H^{\ddagger}$ of 23.8 kcal/mol can be compared with an experimental value of 24.4 kcal/mol[26] and the HF/3-21G value of 35.9 kcal/mol.[8] The calculated $\Delta S^{\ddagger}$ of −44 eu is close to the HF/3-21G ab initio value of −42 eu,[8] and can be compared with the experimental value of −30 eu.[26] The experimental data for this reaction are rather old and are not consistent with more recent results for the reverse reaction (decomposition of cyclohexene) and thermodynamical data.[27] The reverse reaction has an

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[22] Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209.

[23] QCPE Program No. 506.

[24] Our experience with the transition structure optimization routines available in the AMPAC program, NLLSQ and SIGMA, is that they are very inefficient in locating transition structures for systems with many variables, as in the cases reported here. In contrast the method described by Baker (Baker, J. *J. Comp. Chem.* **1986**, *7*, 385) is fast and reliable for finding transition structures and usually also requires less computer time than the default FLEPO method for optimizing ground states. The Baker method has been implemented in the AMPAC program, and the routines are available from the authors upon request. Bitnet/Earn address: FRJ@DKDOU01.

[25] Benson, S. W. *Thermochemical Kinetics*; Wiley: Interscience, 1976.

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Table II. Calculated Relative Energies of Different TS's in the Reaction of Butadiene and Acrolein[a]

method	A	B	C	D
HF/STO-3G[b]	0.0	0.1	0.4	0.7
HF/3-21G[b]	0.0	2.1		
HF/6-31G*[b]	0.0	0.7	0.3	2.0
AM1	0.0	−1.0	−1.1	−1.0

[a] In kilocalories/mole, legends as in Table I. [b] Reference 28.

Table III. Experimental Activation Parameters for the Retro-Diels–Alder Reaction of Substituted Ethanoanthracenes in Diphenyl Ether[a]

reaction	R	$\Delta\Delta G^{\ddagger}$ [b]	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
2b	H	0.0	34.8 ± 1.4	−7.9 ± 2.7
	NH_2	−7.3		
	OPh	−4.5	36.2 ± 1.2	4.6 ± 2.6
	OCH_3	−3.5	32.3 ± 1.0	−5.5 ± 2.2
	CHO	−1.5	40.0 ± 1.1	6.5 ± 2.3
	CH_3	−0.8	37.8 ± 1.9	0.4 ± 3.9
	Cl	+0.2		
	I	+0.2		
	Br	+0.7		
	CO_2CH_3	+1.3		
	NO_2	+3.7		
2c	H	0.0	49.1[c]	12.[c]
	$N(CH_3)_2$	−8.1	29. ± 0.11	−11. ± 0.22
	$N(CH_3)_3^+$	−7.7		
	CHO	−5.7		
	CO_2H	−5.1		
	NH_2	−4.6		
	CN	−4.5		
	CO_2CH_3	−4.2	38. ± 0.38	−1.8 ± 0.74
	NO_2	−2.9		
	OCH_3	−0.8	43. ± 3.4	2.0 ± 6.5
	CH_3	+0.1	44. ± 1.7	2.9 ± 3.2
	$C(CH_3)_3$	+0.3	50. ± 2.0	14. ± 4.0

[a] $\Delta\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$ in kilocalories/mole, $\Delta S^{\ddagger}$ in eu. Values for reaction 2b are taken from ref 7a, values for reaction 2c from ref 7b. [b] $\Delta\Delta G^{\ddagger}$ calculated from relative rates. [c] References 31, 32.

AM1 calculated $\Delta H^{\ddagger}$ of 80.2 kcal/mol and $\Delta S^{\ddagger} = 4.0$ eu, compared to experimental values of $\Delta H^{\ddagger} = 63.7 \pm 2.8$ kcal/mol and $\Delta S^{\ddagger} = 5.9 \pm 5.6$ eu.[27a]

While several ab initio calculations on the reaction of ethylene with butadiene has been reported, only very recently has calculations for an unsymmetrical system, butadiene plus acrolein, appeared.[28] A total of four TS's corresponding to exo and endo configurations and either s-cis or s-trans conformations of acrolein was optimized at the HF/STO-3G level, and the two endo TS's were further refined with the 3-21G basis. Improved relative energies were obtained from single point calculations with the 6-31G* basis. For comparison we have calculated the same reaction with the AM1 method and $\bar{R}_{ts}$ and ΔR_{ts} of the TS's are shown in Table I. The $\bar{R}_{ts}$ differences between AM1 and ab initio values are similar to the butadiene plus ethylene system, and the asymmetries of the HF/STO-3G TS's are reproduced quite closely, but the AM1 relative energies of the four TS's are at variance with the ab initio values (Table II).[16] All the ab initio calculations predict that the endo,s-cis TS should be lowest in energy, in contrast to the AM1 method which places this TS highest in energy. An experimental determination of the endo–exo ratio for this reaction has not been reported, but for the corresponding cyclopentadiene system the endo product is favored by 0.6 kcal/mol.[3] Sodupe et al. have recently reported that AM1 also favor the exo over the endo TS for a cyclopentadiene system, in disagreement with experimental data.[29] They speculate that solvation effects may be the cause of the discrepancy, but in light of the AM1 and ab initio results for the butadiene + acrolein reaction it is more likely that it simply is a failure of the AM1 method. The AM1 disfavoring of the sterically most crowded TS may indicate that the known MNDO overestimation of core–core repulsion at intermediate distances, although reduced with the AM1 method, has not been completely removed. The calculated $\Delta H^{\ddagger}$ of 23.3 kcal/mol is only 0.5 kcal/mol lower than for the butadiene + ethylene reaction. This value is the same as obtained at the ab initio level using the minimal STO-3G basis, but the larger basis sets 3-21G and 6-31G* give more realistic values of 5.4 and 4.0 kcal/mol.[28]

The calculated activation parameters for the retro-DA reaction of bicyclo[2.2.2]octa-2,5-diene to give benzene and ethylene (reaction **1a**, R_2 = H) are $\Delta H^{\ddagger} = 46.2$ kcal/mol and $\Delta S^{\ddagger} = 4.2$ eu while the experimental values are $\Delta H^{\ddagger} = 32.5$ kcal/mol and $\Delta S^{\ddagger} = 3.3$ eu.[30] The reaction is calculated to be concerted and synchronous with the AM1 method since the C_{2v} symmetric TS had exactly one imaginary frequency with the expected atomic motion. The calculated heats of formation of benzene and ethylene are close to the experimental values (errors are 2.2 and 4.0 kcal/mol[15]), and the calculated value for bicyclo[2.2.2]-octa-2,5-diene, 31.5 kcal/mol, is close to the value of 34–35 kcal/mol estimated from experimental data.[30] The calculated $\bar{R}_{ts}$ for this reaction is 2.050 Å, slightly shorter than for the butadiene + ethylene system. The corresponding anthracene reaction **2a** (R_2 = H) has also been investigated experimentally, and the activation parameters determined in diphenyl ether were $\Delta H^{\ddagger} = 49.1$ kcal/mol and $\Delta S^{\ddagger} =$ 12 eu.[31,32] The calculated values are $\Delta H^{\ddagger} = 60.0$ kcal/mol and $\Delta S^{\ddagger} = 5.2$ eu, and the C_{2v} TS has one imaginary frequency. The breaking C–C bond distance is calculated to be 2.133 Å. There is ample evidence in the literature that DA reactions are insensitive to solvent effects (reaction rate differences typical less than a factor of 3 for even large changes in solvent polarity),[3] unless very potent dienophiles like polycyano ethylenes are used, and thus calculated data, which refer to reactions in the gas phase, should be directly comparable to solution-phase data. Judged from these examples, the absolute value of the activation enthalpy for retro-DA reactions appears to be overestimated by the AM1 method by approximately 10 kcal/mol while activation entropies are close to the experimental values. An overestimation of activation energies is typical for ab initio methods based on single determinant wave functions, and electron correlation is necessary for obtaining reasonable agreements with experimental data.[19] Single determinant calculations (ab initio or semiempirical) may still be sufficiently accurate for obtaining substituent effects if the electron correlation error is approximately constant. Only sparse information of whether this is the case is available at present.[33]

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Table IV. Calculated Activation Parameters for Reactions a and b[a]

reaction	R_2	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger\,b}$	$\bar{R}_{ts}$	ΔR_{ts}	$\nu_i^{\,c}$
1a	H	46.2	4.6	2.050	0.0	865
	NH_2	34.9	3.7	2.040	0.0	839
	NO_2	41.8	3.3	2.073	0.0	814
	Cl	43.8		2.051	0.0	
	Br	43.4		2.050	0.0	
	I	44.0		2.047	0.0	
2a	H	60.0	5.2	2.133	0.0	797
	NH_2	47.3		2.126	0.0	
	NO_2	57.3		2.192	0.0	
1b	H	42.5	4.0	2.061	0.238	815
	NH_2	28.3	2.7	2.081	0.373	725
	OCH_3	36.9		2.087	0.387	
	CHO	39.0	2.8	2.057	0.258	814
	CH_3	38.6	5.5	2.066	0.327	800
	Cl	39.8		2.061	0.260	
	I	40.4		2.061	0.315	
	Br	39.8		2.058	0.261	
	NO_2	38.6	3.7	2.067	0.139	814
2b	H	57.2		2.144	0.133	
	NH_2	42.2		2.158	0.206	
	CH_3	53.0		2.147	0.173	
	Cl	53.7		2.145	0.156	
	I	54.7		2.139	0.176	
	Br	54.0		2.142	0.150	
	NO_2	52.0		2.169	0.103	

[a] $\Delta H^{\ddagger}$ in kilocalories/mole, $\Delta S^{\ddagger}$ in eu, $\bar{R}_{ts}$ and ΔR_{ts} in angstroms. [b] Evaluated at $T = 500$ K. [c] Magnitude of imaginary frequency in cm^{-1}.

The retro-DA reaction of 11-substituted and 9,10-disubstituted ethanoanthracenes (reactions 2b and 2c) in diphenyl ether has been studied by Czarnik et al.[7] The only simplification we have made in the computations is the use of a methyl ester instead of an ethyl ester for the reactions 2b. For each of the systems the rate of cycloreversion was determined by UV spectroscopy, and for some substituents the absolute values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were also determined; data relevant for the present study are given in Table III. 9,10-Disubstituted systems show that strongly electron-donating groups accelerate the reaction while strongly electron-withdrawing groups slow the reaction down, in agreement with known substituent effects.[3,2a] There are, however, a few exceptions, e.g. aldehyde groups show a slight accelerating effect even though it normally is considered an electron-withdrawing group (e.g. Hammett σ value of 0.22[34]). The reactivity pattern for 11-substituted systems deviates more from traditional wisdom. Electron-withdrawing groups increase the reaction rate, as expected, but electron-donating groups do not retard the reaction, instead they show almost no effect or in some cases also lower the activation energy. The large stabilization of the NH_2 and $N(CH_3)_2$ groups is clearly unexpected.

While relative rates give relative $\Delta G^{\ddagger}$ ($\Delta\Delta G^{\ddagger}$) accurate to within a few tenths of a kcal/mol, experimental errors for absolute values of activation parameters are much larger. Despite the error limits on $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, there appears to be a correlation between activation enthalpy and activation entropy, with small values of $\Delta H^{\ddagger}$ corresponding to small (negative) values of $\Delta S^{\ddagger}$. This phenomenen has been discussed by Benson and termed the "compensation effect".[25] The energies obtained from AM1 give directly $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ can be calculated by evaluating the vibrational frequencies. Unfortunately the computational procedure does not reproduce the correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, as shown below the calculated activation entropies are almost constant. A comparison between $\Delta\Delta G^{\ddagger}$ values therefore becomes equivalent to a comparison between experimental $\Delta\Delta G^{\ddagger}$ and theoretical $\Delta\Delta H^{\ddagger}$ values. A direct comparison between teoretical and experimental $\Delta\Delta H^{\ddagger}$ values is hampered by the relative large error limits on experimental $\Delta H^{\ddagger}$ values. For the 11-substituted series, however, it is clear that the main contributor to the variation in reaction rate is the change in activation enthalpy (Table III). The data available for the 9,10-disubstituted system make a similar conclusion less certain.

Table V. Calculated Activation Parameters for Reaction c[a]

reaction	R_1	$\Delta H^{\ddagger}$	$\bar{R}_{ts}$	ΔR_{ts}
1c	H	46.2	2.050	0.0
	$N(CH_3)_2$	39.1	2.127	0.538
	$N(CH_3)_3^+$	41.6	2.098	0.428
	CHO	41.6	2.058	0.224
	CO_2H	42.3	2.061	0.248
	NH_2	38.3	2.113	0.488
	NH_3^+	39.5	2.089	0.409
	CN	42.6	2.061	0.227
	CO_2CH_3	42.5	2.061	0.238
	NO_2	41.3	2.076	0.334
	OCH_3	45.2	2.080	0.266
	CH_3	44.7	2.059	0.141
	$C(CH_3)_3$	45.5	2.068	0.187
2c	H	60.0	2.133	0.0
	CHO	55.7	2.140	0.124
	CO_2H	57.0	2.143	0.138
	NH_2	51.3	2.189	0.387
	NH_3^+	52.7	2.159	0.281
	CN	56.7	2.142	0.134
	CO_2CH_3	57.2	2.144	0.133
	NO_2	55.9	2.152	0.198
	OCH_3	59.1	2.163	0.192
	CH_3	58.5	2.142	0.087

[a] $\Delta H^{\ddagger}$ in kilocalories/mole, $\bar{R}_{ts}$ and ΔR_{ts} in angstroms.

The general feature of the transition structures of the substituted systems 1 and 2 is that $\bar{R}_{ts}$ in the anthracene series is approximately 0.08 Å longer than the corresponding distance in the bicyclo series (Table IV and V), and the asymmetry of the TS is more pronounced for the bicyclo series than for the anthracene series. The effect on $\bar{R}_{ts}$ when substituents are introduced is fairly small, being on the order of a few hundreds of an angstrom. For the 9,10-disubstituted systems without an ester group at

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Table VI. Relative $\Delta H^{\ddagger}$ for Reactions a, b, and c[a]

R	1a	2a	1b	2b	$\Delta\Delta G^{\ddagger}_{\mathrm{exp}}$[b]	1c	2c	$\Delta\Delta G^{\ddagger}_{\mathrm{exp}}$[c]
H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NH_2	−11.2	−12.7	−14.2	−15.0	−7.3	−7.8	−8.7	−4.6
OCH_3			−5.6		−3.5	−0.9	−0.9	−0.8
CHO			−3.5		−1.5	−4.5	−4.3	−5.7
CH_3			−3.9	−4.2	−0.8	−1.5	−1.6	+0.1
Cl	−2.4		−2.7	−3.5	+0.2			
I	−2.2		−2.0	−2.5	+0.2			
Br	−2.8		−2.7	−3.2	+0.7			
NO_2	−4.4	−2.7	−3.5	−5.2	+3.7	−4.9	−4.2	−2.9
$N(CH_3)_2$						−7.1		−8.1
$N(CH_3)_3^+$						−4.6		−7.7
CO_2H						−3.9	−3.1	−5.1
NH_3^+						−6.7	−7.4	
CN						−3.6	−3.4	−4.5
CO_2CH_3						−3.7	−2.8	−4.2
$C(CH_3)_3$						−0.7		+0.3

[a] In kilocalories/mole. [b] Experimental $\Delta\Delta G^{\ddagger}$ values for reaction 2b taken from ref 7a. [c] Experimental $\Delta\Delta G^{\ddagger}$ values for reaction 2c taken from ref 7b.

the bridge (reactions labeled a), the NH_2 groups give a slightly shorter $\bar{R}_{ts}$ while the NO_2 groups have the opposite effect. For the unsymmetrical systems b and c, all substituents give $\bar{R}_{ts}$ that is slightly longer than for the unsubstituted case. The degree of elongation shows some correlation with the calculated activation energies, i.e. the more stabilizing substituents have the longer $\bar{R}_{ts}$, but in general the effects are small. The asymmetry of the TS for the 9,10-disubstituted systems b and c, on the other hand, shows a very clear trend that electron-donating groups make the TS more asymmetrical and electron-withdrawing groups have the opposite effect (Table IV). The correlation, however, does not follow the calculated relative activation energies (Table VI), since all substituents are calculated to be stabilizing. The geometries of the TS's show an interesting feature with respect to substituents that have lone pairs (NH_2, OCH_3). The lone pairs of the NH_2 groups are anti and almost exactly aligned with the breaking C–C bonds (i.e. a 180° torsional angle between the lone pairs and the breaking bonds). A corresponding syn TS was found to be 1.7 kcal/mol higher in energy for 1a. The OCH_3 groups show similar features, although in this case only the methoxy group near the ester group (i.e. the longer of the two breaking bonds) has one of its lone pairs parallel to the breaking C–C bond, in this case syn. The 11-substituted systems, reaction c, have calculated asymmetries (Table V) which correlate more closely with the magnitude of the stabilization effects. Also in these cases are the lone pairs of the NH_2 and $N(CH_3)_2$ calculated to eclipse the breaking C–C bond, but the amino groups here have their lone pairs syn. The OCH_3 group gives ambiguous results, for the anthracene system it has one of its lone pairs aligned but not in the bicyclo system. The π-system of the CHO and COOR groups is also found to be aligned with the breaking bond, while the NO_2 group is approximately 20° out of alignment. We note as a curiosum that the magnitude of the imaginary frequency at the TS is remarkably constant, although there is a qualitative correlation with the calculated activation energy (Table IV).[35]

The calculated activation parameters for the reactions are shown in Tables IV and V, and relative values in Table VI. The absolute activation energies for the anthracene system are much larger than for the bicyclo system, but the calculated substituent effects are very similar. When comparing the calculated $\Delta\Delta H^{\ddagger}$ with experimental $\Delta\Delta G^{\ddagger}$ for 9,10-disubstituted systems (Table VI), we note that in all cases the calculated stabilizations are too large, although the trend in reactivity is reproduced fairly well. The major exception is the NO_2 groups, where the calculated stabilization of 5.2 kcal/mol contrasts the observed destabilization of 3.7 kcal/mol. The qualitative wrong prediction for NO_2 clearly illustrate the problem inherent to semiempirical methods. There is nothing in the calculations that indicate that the results for NO_2 should be less reliable than for the other functional groups. The limited data available for experimental $\Delta\Delta H^{\ddagger}$ (Table III) suggest that CHO groups actually are enthalpic destabilizing and that it is the entropy contribution that makes the observed reaction rate slightly faster than for the unsubstituted system. AM1, however, predicts that CHO groups should be energetically stabilizing. The other experimental activation enthalpies are not significantly different from the unsubstituted case to draw similar conclusions. The overall agreement between calculated $\Delta\Delta H^{\ddagger}$ and experimental $\Delta\Delta G^{\ddagger}$ for 11-substituted compounds is somewhat better, the deviations appear to be more or less randomly distributed. The variation in the experimentally determined $\Delta H^{\ddagger}$ values is here somewhat larger than for the 9,10-disubstituted cases, and one can with some confidence conclude that the enthalpic effect to a large extent is offset by the entropic contribution. The free energy stabilization of 4 and 8 kcal/mol found for CO_2CH_3 and $N(CH_3)_2$ is only about half of the enthalpic values. When comparing theoretical and experimental $\Delta\Delta H^{\ddagger}$ values for these two substituents the calculated values thus appear to be too small.

As the entropic contribution to $\Delta\Delta G^{\ddagger}$ is not negligible, and the experimental $\Delta\Delta H^{\ddagger}$ data are scarce and of lower accuracy, neither of the above comparisons is completely satisfactory. Alternatively, one can theoretically calculate the $\Delta S^{\ddagger}$ contribution from vibrational frequencies and directly compare $\Delta\Delta G^{\ddagger}$ values. It is experimentally observed that there is a relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, as discussed above, but the calculated $\Delta S^{\ddagger}$ values are almost constant,[36] as shown in Table IV, thus the inclusion of entropic terms do not improve the agreement with experimental data. The lack of variation in calculated activation entropies is somewhat surprising. The good

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[35] Since the reactions in these cases have very similar TS's, one might expect that the magnitude of the imaginary frequency, which is related to the curvature of the energy surface, would decrease with decreasing activation energy.

[36] The entropic factors in Table IV were evaluated from harmonic vibrational frequencies which is not entirely correct for molecules with internal rotations such as the methyl ester group in reactions b. Deleting these vibrations and using formulas for a free 3-fold rotor instead[25] gave identical activation entropies to within 1 eu.

agreement with experimental values for the parent systems suggest that the AM1 method is quite accurate for calculating vibrational frequencies. Given the variation of the TS geometry with substituents, one might have anticipated a significant variation of activation entropies as well. The almost constant value of ΔS^{*} may possibly be related to the near constant value of $\bar{R}_{ts}$, i.e. all TS's have approximately the same degree of "looseness". A possible explanation for the discrepancy could be that some or all of the reactions considered in this study in fact proceed via a "two-stage" mechanism, as discussed in the "Computational Methods" part.

Finally we would like to note that the above results are not significantly changed by inclusion of termodynamical enthalpy corrections (most importantly zero point energies), which can easily be evaluated from vibrational frequencies. For reaction 1b the substituent effect including these effects are −13.8, −3.3, −3.7, and −3.2 kcal/mol for NH_2, NO_2, CH_3, and CHO, respectively, compared to values of −14.2, −3.5, −3.9, and −3.5 kcal/mol without these corrections, i.e. inclusion of these factors only give insignificant changes.

Summary

The performance of the AM1 method using spin-restricted single-determinant wave functions has been tested for the retro-Diels–Alder reaction of substituted bicyclo[2.2.2]octa-2,5-diene and ethanoanthracene compounds for which experimental data are available. The calculated geometries of the TS's appear quite reasonable when compared to ab initio results. The degree of asynchronicity depends markedly on substituents, with electron donors on the diene component making the TS more, and electron acceptors less, asymmetrical relative to the unsubstituted system. The asymmetry as a function of substituents on the dienophile follow rather closely the calculated TS stabilization. The method, however, is unable to reproduce trends in activation entropies, although absolute values for the parent systems are close to experimental values. A direct comparison between relative activation enthalpies is difficult due to the error limits on the experimental data, but it appears that the method in general predicts a too large stabilization for most substituents. None of the substituents considered here is calculated to be destabilizing, in contrast to experimental data. Nevertheless, trends in reactivity are reproduced surprisingly well, although the qualitatively wrong prediction for some substituents make conclusions based on such calculations regarding reaction mechanisms very prone to errors.

Registry No. **1a** (R_2 = H), 500-23-2; **1b** (R_2 = H), 70209-62-0; **2a** (R_2 = H), 5675-64-9; **2b** (R_2 = H), 13294-86-5.

Meta-Substituent Effects on Benzyl Free-Radical Stability

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A series of 5-substituted 3-cyanotoluenes was synthesized, and the relative rates of *N*-bromosuccinimide bromination were determined in benzene at 80 °C. The resulting $\sigma_F^{\bullet}$ values of meta Me, H, Br, NO_2, and CN were found to be 0.03, 0.00, −0.03, −0.04, and −0.10, respectively. Of these meta substituents, all but methyl were found to be destabilizing to the intermediate benzyl free radical. These meta substituent results are consistent with reported $\sigma_\alpha^{\bullet}$ and $\alpha_c^{\bullet}$ values and cast doubt upon reports that assume meta substituents have no influence on free-radical stability.

The influence of a substituent on the stability of a free-radical intermediate is, in general, less than the corresponding influence of the same substituent on a carbocation or carbanion intermediate. This diminished influence makes quantification more difficult.[1] In the past decade the development of free-radical substituent constants, usually called $\sigma^{\bullet}$, has helped to clarify and quantify free radical substituent effects. A general consensus now exists that some substituents, e.g. para nitro, cyano, acetyl, and phenyl tend to be relatively good at stabilizing a free radical, whereas the stabilizing or destabilizing nature of others, such as para-fluoro and most meta substituents, is still in dispute.

Four new $\sigma^{\bullet}$ scales have appeared since our original $\sigma^{\bullet}$ scale[2] (here called $\sigma_F^{\bullet}$) was developed based on the *N*-bromosuccinimide (NBS) bromination of 4-substituted 3-cyanotoluenes (1). Jackson[3] defined a $\sigma_j^{\bullet}$ scale based on the thermal decomposition of dibenzylmercurials; Arnold[4] used a nonkinetic approach to define the $\sigma_\alpha^{\bullet}$ scale based on esr benzylic α-hydrogen hyperfine coupling constants; Creary[5] chose the thermal rearrangement of 3-aryl-2,2-dimethylmethylenecyclopropanes to 2-arylisopropylidenecyclopropanes to define the $\sigma_c^{\bullet}$ scale; and Jiang[6] developed a $\sigma_T^{\bullet}$ scale based on the cyclodimerization of α,β,β-trifluorostyrenes.

Our quantitative understanding of aryl substituent effects in free-radical reactions has also been enhanced by numerous non-sigma-dot approaches including (a) the thermal decomposition rates of phenylazomethanes,[7]

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