In **1c** the reaction center at position 2 is presumably more crowded because of the presence of three vicinal phenyl groups, which should be forced out of the heteroaromatic cation plane. However, addition is not observed at position 4 of **1c**, where the steric requirements appear to be comparable with those of position 4 of the other cations.

The observed trend in the tendency to undergo nucleophilic addition is consistent with that qualitatively observed for the nucleophilic aromatic substitution of 4-chloro heteroaromatic cations[17] and was subsequently confirmed by kinetic measurements of morpholino demethoxylation of 4-methoxy-2,6-diphenylpyrylium and 4-methoxy-1-methyl-2,6-diphenylpyridinium cations.[18]

It has been suggested that this trend in reactivity corresponds to the increasing contribution of carbonium ion structures in pyridinium, thiopyrylium, and pyrylium cations.[17] Thus the tendency of pyrylium cation to undergo nucleophilic addition is larger than in the other rings just mentioned, because of the presence of the electronegative oxygen atom which causes a strong charge delocalization. ^{13}C NMR data and theoretical calculations of the π-electron charges agree in indicating a lower electron density on the pyrylium ring with respect to the pyridinium ring.[19,20] Resonance formulas such as **6** and **7**, where the positive charge is located on the α or γ carbon atom, visualize satisfactorily the behavior of the pyrylium ring toward nucleophilic reagents.

Acknowledgment. The authors thank Professor G. Illuminati for helpful discussions.

Registry No. 1a, 15959-35-0; **1b**, 18342-83-1; **1c**, 47645-90-9; **1d**, 54231-64-0; **2**, 46897-93-2; **3a**, 71457-44-8; **3b**, 71709-21-2; **3c**, 75102-76-0; **4b**, 71709-22-3; **5**, 75102-77-1; MeO^-, 3315-60-4.

---

(17) Yoneda, S.; Sugimoto, T.; Tanaka, O.; Motiya, Y.; Yoshida, Z. *Tetrahedron* **1975**, *31*, 2669.

(18) Unpublished results from this laboratory.

(19) Balaban, A. T.; Wray, V. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1975**, *30B*, 654.

(20) Palmer, M. H.; Findlay, R. H.; Moyes, W.; Gaskell, A. J. *J. Chem. Soc., Perkin Trans. 2* **1975**, 841.

Rearrangement of 1,1'-Spirobiindene and Thermochemical Evidence for Its Spiroconjugative Destabilization

Richard K. Hill* and Gerald H. Morton

Department of Chemistry, University of Georgia, Athens, Georgia 30602

Donald W. Rogers and Ling S. Choi

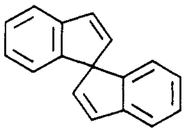
Chemistry Department, Long Island University, Brooklyn, New York 11201

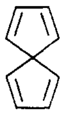
Received July 15, 1980

Thermal rearrangement of 1,1'-spirobiindene (1) in a flow system at temperatures above 300 °C leads exclusively to 3,4-benzofluorene, the product of vinyl migration. The same product is formed by direct irradiation at 254 nm or by treatment with potassium in refluxing THF. Determination of the heats of hydrogenation of 1 (–61.0 kcal/mol) and indene (–23.63 kcal/mol) reveals a destabilization in 1 of 13.7 kcal/mol relative to indene, in agreement with literature calculations that spiroconjugated systems like 1 possess high strain energies attributable to unfavorable π-orbital interactions.

Previous papers in this series have provided evidence that 1,1'-spirobiindene (**1**) is a spiroconjugated[1] molecule: the ultraviolet spectrum[2] exhibits a strong bathochromic shift compared to that of indene; the NMR spectrum[2] shows an upfield shift for the C-2 proton compared to simple indenes; the ORD spectrum[2] displays an intense Cotton effect at 233 nm; and, most importantly, the photoelectron spectrum[3] shows a splitting of the indene bands which correlates quantitatively with splittings in other spiroconjugated systems.

The present investigation was undertaken to add some knowledge of chemical stability to these spectroscopic investigations. Spiroconjugation does not automatically confer stabilization on a molecule, particularly when, as in the case of **1** and the parent spiro[4.4]nonatetraene (**2**),[4] the spiroconjugated system is a $4n$ π network. Indeed, molecular orbital calculations on **2** have reached contradictory conclusions on the consequences of spiroconjugation. Using CNDO/2 calculations, Tajiri and Nakajima[5] concluded that spiroconjugation has little, if any, contribution to the stabilization of molecules like **2** in their ground state. On the other hand, Gordon et al.[6] concluded on the basis of CNDO/2, MINDO/3, and SPINDO calculations that spiroconjugation should impart a net stabilization to **2**. The opposite conclusion was reached by Kao and Radom[7] from ab initio (STO-3G) calculations; they argued that the HOMO–HOMO interaction between the two butadiene fragments of **2** involves four electrons and is net destabilizing. Finally, Houk et al.[8] have recently come to the broader conclusion that homoconjugative interactions in general between neutral closed-shell π systems are destabilizing.


1


2

We have studied the stability of **1** toward pyrolysis,

---

(1) Simmons, H. W.; Fukunaga, T. *J. Am. Chem. Soc.* **1967**, *89*, 5208. Hoffman, R.; Imamura, A.; Zeiss, G. D. *Ibid.* **1967**, *89*, 5215. Dürr, H; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 559.

(2) Hill, R. K.; Cullison, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 1229.

(3) Schweig, A.; Weidner, U.; Hill, R. K.; Cullison, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 5426.

(4) Semmelhack, M. F.; Foos, J. S.; Katz, S. *J. Am. Chem. Soc.* **1973**, *95*, 7325.

(5) Tajiri, A.; Nakajima, T. *Tetrahedron* **1971**, *27*, 6089.

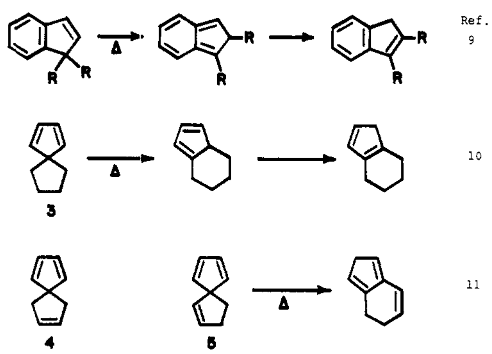
(6) Gordon, M. D.; Fukunaga, T.; Simmons, H. E. *J. Am. Chem. Soc.* **1976**, *98*, 8401.

(7) Kao, J.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 760.

(8) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797.

0022-3263/80/1945-5163$01.00/0

Scheme I. Thermal Rearrangements of Disubstituted Indenes and Cyclopentadienes



Scheme II. Thermal Rearrangement of 1

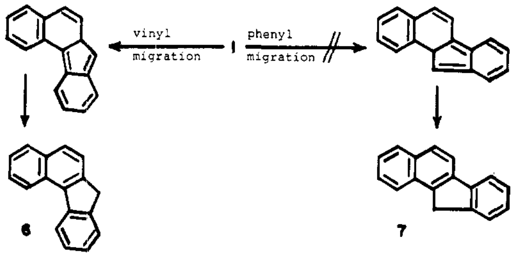


Table I. Pyrolysis of 1,1'-Spirobiindene

temp, °C	% rearrangement
270	10
330	30
370	38
450	53
475	86

photolysis, and some chemical reagents and have also attempted to provide quantitative evidence for spiroconjugative stabilization or destabilization by determination of the heat of hydrogenation.

Pyrolysis. Thermal rearrangement of 1,1-disubstituted indenes and 5,5-disubstituted cyclopentadienes normally involves a 1,5-alkyl or -aryl shift followed by a 1,5-hydrogen shift, as illustrated by the examples in Scheme I. The alkyl or aryl migration step in the rearrangement of both the indene and cyclopentadiene series has been concluded to be a concerted sigmatropic 1,5-rearrangement.[9,10] Semmelhack[4] found that rearrangement of 2 to indene had a half-life of 66 min at 65 °C and an activation energy about 10 kcal less than that of 3 or 4, suggesting that 2 was less stable than its reduced relatives 3 and 4.

Analogous rearrangement of spiroindene 1 could involve migration of either the vinyl or the phenyl group, as shown in Scheme II. Experimentally, the sole rearrangement product observed was 3,4-benzofluorene (6), the product of vinyl migration. It may be noted that pyrolysis of 5 also involves preferential vinyl migration.[11]

1,1'-Spirobiindene was rearranged by passing a solution of the hydrocarbon, under a flow of helium, through a glass bead packed vertical Pyrex column. Table I shows the degree of rearrangement (analyzed by NMR) as a function of temperature.

Photolysis. Spirobiindene 1 was found to rearrange rapidly and almost quantitatively to 6 when irradiated with a low-pressure Hg-vapor lamp at 253.7 nm. This isomerization can be interpreted as an example of the di-π-methane rearrangement, as shown in Scheme III. The first step is postulated to be the divinylmethane rearrangement to 8, analogous to the photorearrangements of 10 to 11[12] and 12 to 13.[13] Both of these latter rearrangements were deduced to occur via excited singlet states, and it is likely that 1 rearranges in the same manner. Intermediate 8 (or the diradical precursor to the cyclopropane ring) can isomerize to isoindene[14] 9, which then aromatizes to the stable benzfluorene 6 by 1,5-hydrogen transfer. Other mechanisms[15] are conceivable and cannot be ruled out without further evidence. The divinylmethane mechanism has the virtue of neatly accounting for the exclusive vinyl migration to form 6 rather than 7.

Scheme III. Photorearrangement of 1

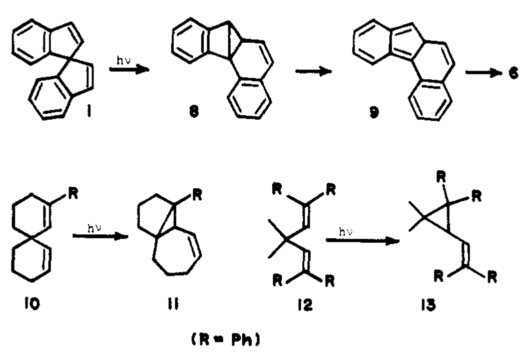


Table II. Heat of Partial Hydrogenation of 1,1'-Spirobiindene (1)

	$\Delta H_{\mathrm{hydrog}}$, kcal/mol
1 vs. 1-hexene	−61.06 ± 1.1
1 vs. 1-hexene	−60.87 ± 1.2
1 vs. 1-indene	−61.23 ± 0.7
mean	−61.0 ± 1.0

Other Rearrangements. Rearrangement of 1,1-diarylindenes can be effected by alkali metals.[16] Spiroindene 1 is relatively stable to lithium or sodium (less than 10% rearrangement in refluxing THF for 3 days) but was converted to 6 in high yield in a refluxing solution in THF with potassium for 24 h.

Surprisingly, 1 was quite stable to attempted acid-catalyzed rearrangement. Heating in PPA at 145 °C for 20 h gave no rearrangement products, and 1 was recovered unchanged after treatment with p-toluenesulfonic acid in CCl_3COOH at 130–145 °C for 2 weeks.

Heat of Hydrogenation. To provide a more quantitative measure of the influence of spiroconjugation on stabilization of 1, the heat of hydrogenation of the nonaromatic double bond was determined as well as that of indene, as a standard for comparison. The literature contains no direct measurement of the heat of hydrogenation of the nonaromatic double bond in indene, but Kistiakowsky's group obtained precise data on the total hydrogenation of indene and indane[17] from which the desired value may be calculated by difference. These data, however, were obtained at 100 °C and corrected to 82 °C by using Kirchoff's equation,[18] taking $-\Delta C_p$ to be 4 cal

---

[9] Miller, L. L.; Boyer, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 650.

[10] Dane, L. M.; de Haan, J. W.; Kloosterziel, H.; *Tetrahedron Lett.* **1970**, 2755.

[11] Semmelhack, M. F.; Weller, H. N.; Clardy, J. *J. Org. Chem.* **1978**, *43*, 3791.

[12] Mariano, P. S.; Steitle, R. B.; Watson, D. G.; Peters, M. J.; Bay, E. *J. Am. Chem. Soc.* **1976**, *98*, 5899.

[13] Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718.

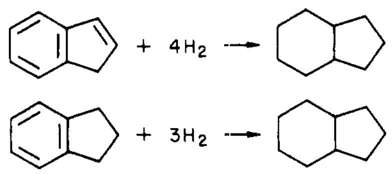
[14] McCullough, J. J.; Yarwood, A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 485.

[15] Padwa, A.; Goldstein, S.; Loza, R.; Pulwer, M. *Tetrahedron Lett.* **1979**, 4895. Giacherio, D.; Morrison, H. *J. Am. Chem. Soc.* **1978**, *100*, 7109 and earlier papers.

[16] Miller, L. L.; Boyer, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 646 and references therein.

[17] Dolliver, M. A.; Gresham, T. L.; Kistiakowsky, G. B.; Vaughan, W. E. *J. Am. Chem. Soc.* **1937**, *59*, 831.

mol^{-1} K^{-1} for each double bond reduced. For comparison with our direct measurment at 25 °C, we have used this treatment to extrapolate his data to 25 °C; while there is certainly some error introduced by applying this correction factor over a range of 75 °C, the larger of the two corrections is only 0.9 kcal/mol, so that an error as large as 10% would not seriously compromise the data. The values obtained are shown below. The difference between the heats of hydrogenation of indene and indane, −23.78 kcal/mol, corresponds to the partial heat of hydrogenation of indene to indane at 25 °C.



	ΔH_{hydrog}, kcal/mol,[17] extrapolated to	
	82 °C	25 °C
+ $4H_2$ →	−69.91	−68.99
+ $3H_2$ →	−45.80	−45.21

By use of the apparatus described previously for determination of heats of hydrogenation on microsamples at room temperature,[19] the heat of hydrogenation of the nonaromatic double bond of indene was measured directly on two samples of purified indene from different sources. The values obtained were −23.71 ± 0.24 and −23.54 ± 0.43 kcal/mol; the uncertainties are 95% confidence limits on nine sequential runs using 40-μL aliquots of the same solution. The mean value, −23.63 ± 0.33 kcal/mol, is not statistically different from the value extrapolated from Kistiakowsky's data and lends confidence to the accuracy of this method.

The heat of hydrogenation of 1,1'-spirobiindene was determined in three separate experiments, each consisting of nine runs, two using 1-hexene as a standard and one using indene as the standard. The results are shown in Table II. The uncertainties given are 95% confidence limits for eight degrees of freedom.

Possible errors due to weighing and handling small samples are not included in the uncertainties given above and may make the total experimental uncertainty as high as ±2 kcal/mol as a "worst case" estimate. Nevertheless, the results clearly show that a substantial destabilizing effect ensues by linking two indene units in spiro fashion. The data show this effect to be of the order of 61.0 − 2(23.63) = 13.7 kcal/mol.

This remarkable destabilization observed experimentally strongly supports the conclusions of Kao and Radom,[7] who calculated a strain energy of 18.1 kcal/mol for spirane **2**, 6.3 kcal/mol higher than the sum of the strain energies of two separate cyclopentadiene rings. They attributed the strain energy to unfavorable π-orbital interactions in the rigid spiro system. These intractions should be magnified in the spirobiindene **1**, and the resulting strain energy appears to be the primary reason for the relative destabilization in **1**.

Experimental Section

Melting points were determined in a Hoover capillary melting point apparatus and are uncorrected. Proton NMR spectra were recorded on a Varian T-60 spectrometer, while ^{13}C NMR spectra were recorded by Mr. Courtney Pape on a JEOL PFT-100 instrument. Infrared (IR) spectra were recorded on a Perkin-Elmer 237B spectrophotometer, and ultraviolet (UV) spectra were recorded on a Beckman Model 25 spectrophotometer. Tetrahydrofuran (THF) was dried by distillation from potassium, and ether was distilled from lithium aluminum hydride. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

1,1'-Spirobiindene (1). This was prepared as described by Hill and Cullison,[2] using the dehyrobromination procedure (b) as the final step. The spirane was chromatographed on alumina with petroleum ether and distilled, bp 90–94 °C (0.01 mm). The IR, UV, and ^{1}H NMR spectra were identical with those reported;[2] ^{13}C NMR (CDCl$_3$) δ 144.538, 143.562, 137.042, 132.711, 126.800, 125.215, 121.679, 120.704, 70.228.

Thermal Rearrangement. The run at 450 °C is described. A solution of 0.99 g of **1** in 2.0 mL of ether was placed in a small addition funnel and slowly dropped through a vertical Pyrex column (70 cm, 7-mm i.d.) packed with 4-mm hollow glass beads and heated to 450 °C. A steady flow of helium was maintained during addition and until the column had cooled. The pyrolysate (1.1 g) was collected in an ice–water trap followed by two dry ice–acetone traps. Analysis of the NMR spectrum indicated that the pyrolysate was 50% recovered **1** and 50% rearranged hydrocarbon.

Recrystallization from methanol gave, in two crops, 0.529 g of gray crystals, mp 122–123 °C (0.408 g) and mp 120–121 °C (0.121 g). Concentration of the filtrate gave 0.57 g of recovered **1**, nearly pure by NMR.

The crystalline product was converted to the picrate, red needles, mp 130.5–131.5 °C (lit.[20] mp 131.4–132.2 °C). Decomposition of the picrate with ammonia left 3,4-benzofluorene (**6**) which, after recrystallization from ethanol, gave colorless plates: mp 124–125 °C (lit.[20,21] mp 124–125 °C, 126.8–127.4 °C). The IR spectrum [(KBr) 3045, 1520, 1470, 1455, 1390, 1370, 1340, 1320, 1260, 1210, 1190, 1100, 1020, 940, 860, 850, 800, 782, 750, 735, 708 cm^{-1}] was identical with the published spectrum:[22] NMR (CDCl$_3$) δ 8.18 (1 H, d, aromatic), 8.4 (1 H, d, aromatic), 7.3–8 (8 H, m, aromatic), 3.9 (2 H, s, CH$_2$); UV (cyclohexane) 216 nm (ϵ 25 500), 233 (42 000), 253 (18 200), 264 (18 700), 300 (9700), 312 (12 500), 321 (10 100), 329 (8095), 336 (13 560). The 1,3,5-trinitrobenzene adduct, prepared in 1:1 benzene–ethanol, gave orange-yellow crystals, mp 153.5–154 °C (lit.[20] mp 154.2–155.2 °C). The 2,4,7-trinitrofluorenone adduct crystallized from 1:1 benzene–ethanol as red needles, mp 191–192 °C (lit.[20] mp 191.8–192.8 °C).

Photochemical Rearrangement. Spirobiindene **1** (216 mg) was photolyzed in 1 L of nanograde hexanes (10^{-3} M) at room temperature under a helium atmosphere for 15 min, using a low-pressure Hg arc (253.7 nm) and quartz glassware. Removal of solvent on a rotary evaporator gave 224 mg of a light yellow solid, mp 110–115 °C. Development of the product and a spirobiindene–3,4-benzofluorene mixture on the same silica gel TLC strip with cyclohexane showed that the major product had the same R_f value as 3,4-benzofluorene and showed the presence of a trace of material with the same R_f value as **1**. Recrystallization from ethanol gave 175 mg of 3,4-benzofluorene: mp 123–125 °C; picrate, mp 130–131 °C; IR and NMR spectra identical with spectra obtained from the thermally rearranged material. A second crop of 35 mg was obtained, mp 120–122 °C, giving a total yield of 97%.

Alkali Metal Rearrangement of 1. A solution of **1** (216 mg) in 12 mL of dry THF under a nitrogen atmosphere was treated with potassium (118 mg) and heated to reflux for 24 h. After cooling, the reaction mixture was quenched with wet THF, concentrated, diluted with ether, and washed with dilute HCl. Drying over MgSO$_4$ and concentration left 205 mg of a yellow solid, which was recrystallized from ethanol to afford 194 mg (90%) of 3,4-benzofluorene (**6**), mp 123–125 °C, identical by IR, NMR, and mixture melting point with the samples obtained above.

Heat of Hydrogenation. The apparatus and procedure have been previously described.[19] Both the 1-hexene used as standard and one sample of indene were obtained from Chemical Samples

---

[18] Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: London, 1970; p 14.

[19] Rogers, D. W.; Papadimetriou, P. M.; Siddiqui, N. A. *Mikrochim. Acta* **1975**, 389. Rogers, D. W.; Dagdagan, O. A.; Allinger, N. L. *J. Am. Chem. Soc.* **1979**, *101*, 671.

[20] Orchin, M.; Friedel, R. A. *J. Am. Chem. Soc.* **1949**, *71*, 3002.

[21] Cook, J. W.; Dansi, A.; Hewett, C. L.; Iball, J; Mayneord, M. V.; Roe, E. *J. Chem. Soc.* **1935**, 1319.

[22] American Petroleum Institute Research Project 44, no. 2307.

Co.; the second indene sample was obtained from Neville Chemical Co. and was twice distilled, taking the middle cut each time. The poduct was isolated to confirm that only the nonaromatic double bonds of 1 were reduced during the heat of hydrogenation determination. IR, UV, and NMR spectra, as well as GC retention time, confirmed its identity with 1,1'-spirobiindane.[2]

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.41; H, 7.54.

Registry No. 1, 165-42-4; 6, 205-12-9; 6·picrate, 70667-77-5; 6·1,3,5-trinitrobenzene, 75299-14-8; 6·2,4,7-trinitrofluorenone, 75311-34-1.

Effects of Alkyl Groups on Rates of Acyl-Transfer Reactions

DeLos F. DeTar

Department of Chemistry, Florida State University, Tallahassee, Florida 32306

Received April 8, 1980

The Taft equation in σ_1 (or σ^*) and E_s has been examined critically for two major purposes: to provide a definitive evaluation of the significance of polar or other nonsteric effects of alkyl groups and to determine what types of steric effects can be correlated among acyl-transfer reactions. The evaluation has led to several conclusions of general interest. (1) The σ^* values of alkyl groups are an artifact; they represent a residual steric effect plus an error component. (2) The apparent need for the $\rho_I\sigma_I$ term or other nonsteric term for alkyl groups is also an artifact. (3) A recent sophisticated statistical analysis which purports to show a need for a nonsteric $\beta_2\theta_2$ term is based on a seriously flawed data set. (4) Proposed alternatives to E_s such as E_s^c, υ, or θ_2 are without special merit and should be abandoned. (5) The Dubois E_s' values extend the E_s set but are based on a slightly different scale. Except for values which correct erroneous experimental data, correlations with the E_s' (Dubois) set are comparable to correlations with the E_s (Taft) set. (6) Procedures are suggested and implemented for reevaluating E_s values and for determining new E_s values. (7) The Taft equation is applicable to steric effects in the alkoxyl group and in the entering nucleophile as well as in the acyl group. (8) All types of acyl-transfer reactions are, in principle, suitable for the measurement of steric effects of alkyl groups. (9) Variations in the ρ_s constant are interpreted in terms of limitations on additivity of steric effects.

Although steric effects play a major role in controlling rates of reactions, research on steric influences has been discouraged by recognition of the possibility of nonadditivity and by doubts about the validity of the available linear free-energy relationships (LFER's).[1-3] Recent developments in the theoretical computation of steric effects on reaction rates promise to provide a firm theoretical underpinning.[4-8] Further progress will depend on new experimental efforts designed to improve the reliability of the data for sterically crowded reactants and to extend the range and the variety of steric effects for which quantitative values are available.

There is also a major role for empirical LFER treatments of steric effects. It becomes of interest, therefore, to carry out a detailed critical evaluation of the presently available LFER treatments in order to assess the importance of nonsteric effects and to point up a number of potentially useful extensions.

It has been recognized that four major factors determine the reactivity of a functional group. These have usually been identified as polar, steric, resonance, and solvation.[1-3] Steric effects and solvation are clearly through-space effects and for several systems polar effects have been computed theoretically as through-space effects by the Kirkwood–Westheimer equation or by related expressions.[9-13] Resonance effects are through-bond effects, but there are other through-bond effects, and the more general term bonding effects may be used to designate all types. A bonding effect is a through-bond effect that alters the free energy of formation of a molecule or of a transition state. Hyperconjugation is a further example.[2,14] Less well recognized is the branching effect which alters enthalpies of formation as in the pentane series: $\Delta H_f = -35.0$ (pentane), -36.9 (2-methylbutane), and -39.7 kcal/mol (2,2-dimethylpropane).[15] Additional examples are to be found in S_N2 reactions,[16] and an example directly pertinent to acyl transfer is given below.

Interactions among the several effects can lead to complexities, but if the main effects can be sufficiently well isolated, then interactions become relatively unimportant.

The proper sorting out of polar effects has long been a goal;[1-3,17,18] we propose instead to sort out steric effects. The primary emphasis is on alkyl groups and on cycloalkyl systems since these constitute a particularly rich popula-

---

(1) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, 1956, p 556.

(2) C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, **2**, 323–400 (1964).

(3) J. Shorter, *Q. Rev., Chem. Soc.*, **24**, 433–453 (1970).

(4) R. C. Bingham and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93**, 3189–3199 (1971).

(5) D. F. DeTar and C. J. Tenpas, *J. Am. Chem. Soc.*, **98**, 4567–4571 (1976); **98**, 7903–7908 (1976).

(6) P. Müller and J. C. Perlberger, *J. Am. Chem. Soc.*, **98**, 8407–8413 (1976); J. C. Perlberger and P. Müller, *ibid*, **99**, 6316–6319 (1977).

(7) D. F. DeTar, D. F. McMullen, and N. P. Luthra, *J. Am. Chem. Soc.*, **100**, 2484–2493 (1978).

(8) D. F. DeTar and N. P. Luthra, *J. Am. Chem. Soc.*, **102**, 4505 (1980).

(9) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938).

(10) F. H. Westheimer and J. G. Kirkwood, *J. Chem. Phys.*, **6**, 513 (1938).

(11) F. W. Baker, R. C. Parish, and L. M. Stock, *J. Am. Chem. Soc.*, **89**, 5677 (1967).

(12) C. F. Wilcox and C. Leung, *J. Am. Chem. Soc.*, **90**, 336 (1968).

(13) S. Ehrenson, *J. Am. Chem. Soc.*, **98**, 7510 (1976).

(14) D. J. DeFrees, M. Taagepera, B. A. Levi, S. K. Pollack, K. D. Summerhays, R. W. Taft, M. Wolfsberg, and W. J. Hehre, *J. Am. Chem. Soc.*, **101**, 5532–5536 (1979).

(15) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, 1969.

(16) D. F. DeTar, *J. Org. Chem.*, following paper in this issue.

(17) S. Ehrenson, R. T. C. Brownlee, and R. W. Taft, *Prog. Phys. Org. Chem.*, **10**, 1 (1973).

(18) N. B. Champman and J. Shorter, Eds., "Correlation Analysis in Chemistry", Plenum Press, New York, 1978.

0022-3263/80/1945-5166$01.00/0