trapping and nitro migration. However, data available so far are consistent with the assumption of essentially complete trapping.

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(13) Ipso partial rate factors in benzo-fused bi- and tricyclic systems currently are under separate study, and will be reported in due course.

(14) Nitrations of **2-4** with copper nitrate-acetic anhydride are not clean; benzonorbornadiene, in particular, gives considerable amounts of products derivable at least in part from reaction of the isolated double bond. Introduction of the nitro group, however, appears to stabilize nitro derivatives toward further electrophilic attack. Side reactions of **2-4** do not affect the data presented.

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(18) A referee has suggested that preferential ipso attack at C_3 in **7** can be explained by cyclopropane stabilization of a Wheland-type transition state, which would invalidate this reaction as a useful precedent for inductive deactivation of an ipso position by cyclopropyl. We note that (a) there is evidence to indicate that the cyclopropane ring in **7** is in nearly the worst possible geometry for conjugative interaction with the benzene π system,[19] and (b) this situation is not greatly improved in the Wheland intermediate (model inspection). Thus, in our view, inductive deactivation by cyclopropyl remains a viable factor in nitration of **7**.

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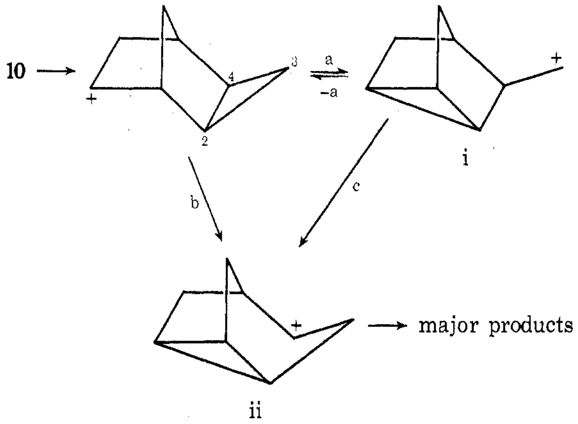
(23) The question of relative magnitudes of 2,3- and 2,4-bond participation has been raised by a referee. Studies[24,25] of a reaction which generates a stereoelectronically similar system (solvolysis of brosylate **10**; see text) can be interpreted as sources of evidence for either mode of participation, depending on whether one regards step b or steps (a + c) as a more facile route to species ii (below). Our preference for step b is based on the facts that i is a primary cation whereas ii is secondary, and cyclopropyl σ-route migration to a C^+ center (step c) is not facile relative to processes involving C-C ring bonds (see comments in ref 25).



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Estimations of van der Waals Strain in Hydrocarbons

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Evaluation of van der Waals strain can in principle be based on enthalpies of formation of appropriate reference compounds. However, experimental enthalpies are available for molecules exhibiting only relatively restricted ranges of crowding. A potentially useful source of further data may be found in relative reaction rates of crowded molecules.

Recent studies have shown encouraging success in calculating steric retardation and steric acceleration.[1-6] These have been based ultimately on calculation of enthalpies of formation of model compounds, and more specifically on calculation of relative differences in strain energy between some model of the reactant system and some model of the transition state.

A wide variety of methods has been proposed for estimating enthalpies of formation of alkanes and cycloalkanes; these are, of course, methods of interpolation and extrapolation from experimental values.[7-17]

We have made a careful evaluation of four representative methods for estimating the strain energy component of alkanes (primarily van der Waals) and have explored the usefulness of two criteria for judging effectiveness: (1) the accuracy with which the method reproduces experimental $\Delta H_f{}^0$ values, and (2) the accuracy with which it treats relative rates of reactions controlled primarily by steric factors. We conclude that accuracy of reproducing $\Delta H_f{}^0$ values is at present an insufficient criterion; methods which are expected a priori to give a poor account of strain energy may yield quite good $\Delta H_f{}^0$ values. The problem lies in three facts: (1) that for alkanes the strain energy component is a small (and variable) fraction of the total $\Delta H_f{}^0$, (2) that the six or more adjustable constants employed in each method tend to absorb the strain components in nonspecific ways, and (3) that accurate experimental $\Delta H_f{}^0$ values exist for rather few strained molecules, the available data making relatively modest demands on any method of calculating $\Delta H_f{}^0$. We have evaluated the Franklin protocol,[15] a simple and relatively effective older method which treats strain effects very roughly, the Allen protocol,[16,17] which reproduces experimental $\Delta H_f{}^0$ values well, and molecular mechanics using two of the several available good alkane force fields, Allinger 1971[13] and Schleyer 1973.[12] The list we have treated includes most of the alkanes and methyl-substituted alkanes for which accurate experimental $\Delta H_f{}^0$ values are reported.[9] The results are shown in Figures 1a–c. The standard deviations and correlation coefficients are as follows: Franklin, 0.6, 0.998; Allen, 0.3, 0.999; Schleyer, 0.7, 0.998; Allinger (not shown), 0.4, 0.999. The molecular mechanics data are based on our calculations (a) of steric energies, (b) of statistical mechanical corrections,[18] and (c) of reparameterized group increment values.[5] Each of the four methods does a good job overall in predicting $\Delta H_f{}^0$ for the reference compounds. The problem may now be presented by reference to Figures 2a–c. These show what happens when a series of considerably more hindered alkanes is treated by the same methods. Each point in Figure 2 is based on a difference, $\Delta\Delta H_f{}^0 = \Delta H_f{}^0[\mathrm{RC(CH_3)_3}] - \Delta H_f{}^0[\mathrm{RCH(CH_3)_2}]$ for a neoalkane and an isoalkane. Experimental data are available for just a few of the 36–40 alkanes represented in the figure. The log k_{rel} are the Taft E_s values representing steric hindrance;[19] $k_{\mathrm{rel}} = k/k_0$ where k is rate of hydrolysis of any ester RCOOEt

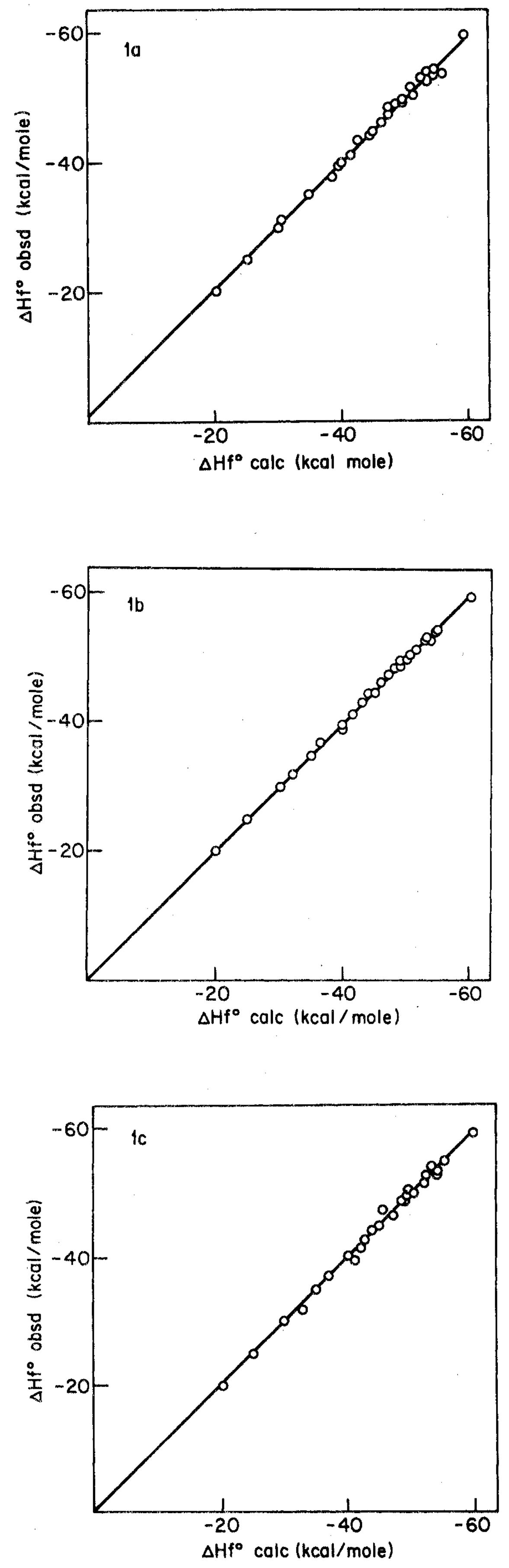

Figure 1. Observed heat of formation (ΔH_f^0) vs. calculated heat of formation (gas, 298 °C) for various alkanes; (a) using Franklin protocol,[15] (b) using Allen protocol,[16,17] (c) using molecular mechanics with Schleyer 1973[12] force field.[5,6] The Allinger 1971 force field gives a generally comparable plot. These data are from ref 6.

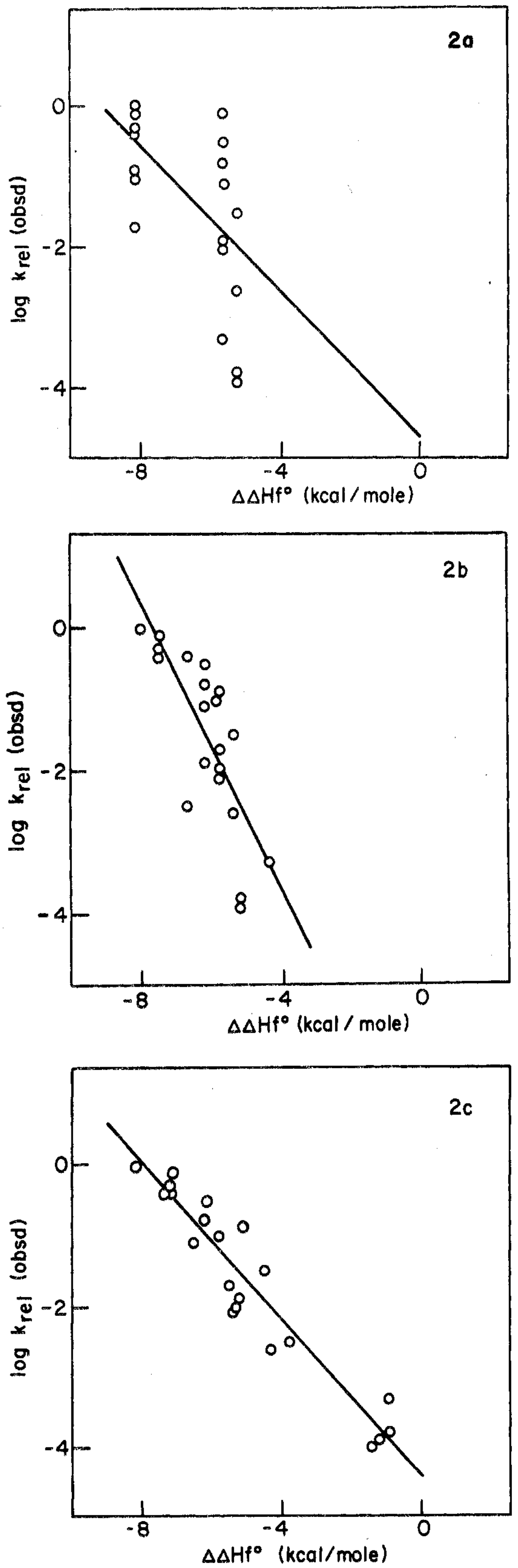

Figure 2. The strain energy component of the calculated ΔH_f^0 values of Figure 1 as shown by plot of Taft E_S values ($-\log k_{rel}$)[18] vs. $\Delta\Delta H_f^0$ where $\Delta\Delta H_f^0 = \Delta H_f^0$ (neoalkane) $- \Delta H_f^0$ (isoalkane); using ΔH_f^0 calculated (a) by the Franklin protocol, (b) by the Allen protocol, and (c) by molecular mechanics with the Schleyer force field. The Allinger 1971 force field gives a generally comparable plot. In 2c we have omitted points for cyclobutanecarboxylic acid and for cyclopentanecarboxylic acid, for which the isoalkane–neoalkane model breaks down, and for dineopentylacetic acid, for which the Schleyer and the Allinger force field calculation fails on the model hydrocarbons. The data are from ref 6.

Table I. Alkanes Used to Get Calibration Terms

	Registry no.	$-\Delta H_f^0$ (298)[a] exptl	SM[b]	Lowest[d] energy conformer Exptl	Lowest[d] energy conformer Calcd	"Exptl"[e] strain energy	SE[f] (Schleyer)	SE[g] strainless (Schleyer)	SE[h] (Allinger)	SE[i] strainless (Allinger)
Pentane	109-66-0	−35.00	0.39	−35.39	−35.46	0.07	2.94	2.92	4.33	4.34
Hexane	110-54-3	−39.96	0.63	−40.59	−40.61	0.02	3.52	3.50	4.95	4.95
Heptane	142-82-5	−44.88	0.86	−45.74	−45.77	0.03	4.10	4.07	5.56	5.56
Octane	111-65-9	−49.82	1.10	−50.92	−50.92	0.00	4.67	4.64	6.17	6.17
Nonane	111-84-2	−54.74	1.33	−56.07	−56.07	0.00	5.24	5.21	6.77	6.78
Decane	124-18-5	−59.67	1.57	−61.24	−61.22	−0.02	5.81	5.79	7.38	7.39
Undecane	1120-21-4	−64.60	1.80	−66.40	−66.38	−0.02				
Dodecane	112-40-3	−69.52	2.04	−71.56	−71.53	−0.03				
2-MeC4	78-78-4	−36.92	0.09	−37.01	−37.55	0.54	3.80	3.08	3.47	2.78
2-MeC5	107-83-5	−41.66	0.27	−41.93	−42.71	0.78	4.38	3.65	4.11	3.39
2-MeC6	591-76-4	−46.59	0.52	−47.11	−47.86	0.75	4.93	4.23	4.69	4.00
2-MeC7	592-27-8	−51.50	0.76	−52.26	−53.01	0.75	5.50	4.80	5.30	4.61
2,2-Di-MeC4	75-83-2	−44.35	0.00	−44.35	−45.69	1.34	5.03	3.62	1.91	0.53
2,2-Di-MeC5	590-35-2	−49.27	0.12	−49.39	−50.85	1.46	5.59	4.20	2.55	1.14

[a] References 9–11. [b] Statistical mechanical correction, ref 18. [c] Column 2 − column 3, "experimental" energy of conformer of lowest energy. [d] $-10.000\, n(\mathrm{CH_3}) - 5.153\, n(\mathrm{CH_2}) - 2.400\, n(\mathrm{CH}) - 0.540\, n(\mathrm{C})$. [e] Nominal values are 0 for n-alkanes, 0.70 for isoalkanes, 1.40 for neoalkanes. Deviations from the nominal represent experimental error or departures from the assumed model. [f] Steric energy from Schleyer 1973 force field, ref 12. [g] $0.602\, n(\mathrm{CH_3}) + 0.573\, n(\mathrm{CH_2}) + 0.700\, n(\mathrm{CH}) + 0.643\, n(\mathrm{C})$. The difference between the SE columns should match the value in the exptl strain energy column. [h] From Allinger 1971 force field, ref 13. [i] $1.254\, n(\mathrm{CH_3}) + 0.610\, n(\mathrm{CH_2}) - 1.595\, n(\mathrm{CH}) - 5.101\, n(\mathrm{C})$.

and k_0 is the corresponding rate for ethyl acetate. The neoalkane has been taken as a model of the transition state in formation of tetrahedral intermediate, the isoalkane as model of the starting ester. Remarkably enough the energy differences, $\Delta\Delta H_f^0$, calculated by molecular mechanics for these alkanes in the gas phase show a good correlation with ester hydrolysis rates.[5]

Use of better models, RCOOH and $\mathrm{RC(OH)_3}$, respectively, gives even better correlations.[6] However, these better models unfortunately require introduction of several ad hoc constants into the alkane force fields. (The Franklin and Allen protocols are not applicable to these oxygen-containing models.)

It is relatively clear from Figure 2 and verifiable by the statistics that molecular mechanics ΔH_f^0 values based on the Schleyer force field, though showing the poorest correlation with ΔH_f^0 experimentally, are greatly superior to the empirical Allen protocol values when applied to these highly hindered compounds. Results are as follows: Franklin protocol correlation coefficient, −0.57; Allen, −0.76; Schleyer, −0.95; Allinger, −0.93.

Results and Discussion

There have been many definitions of strain energy;[12–14] most are based on ΔH_f^0 values for the first members of the alkane series. Since for present purposes it is clearly necessary to seek the highest possible precision, we have explored a modified definition of strain based on the alkanes listed in Table I. In our definition, all strain values are related to the n-alkane single conformation of lowest energy and make use of an extended set of statistical mechanical corrections.[18] We define strain as follows: n-alkane, fully extended, zero strain; isoalkane, 0.70 kcal/mol; terminal neoalkane, 1.40 kcal/mol. These values are consistent with differences in observed enthalpies.[9] There are certain advantages in skipping over the first members of each series since these prove exceptional when enthalpy correlations are attempted.[9]

The column labeled "Exptl" strain energy shows how small are the deviations of calculated strain from the defined strain values of 0, 0.70, and 1.40; the standard deviation is about 0.06 kcal/mol. The group increment values in footnote d therefore provides a good account of the strain-free component of ΔH_f^0 for alkanes.

A molecular mechanics calculation leads to a "steric energy" for a given conformation. The steric energy may be dissected into a strain energy component and a "base" energy component which may be computed from the usual group increments. The "base" component depends on how the force field has been defined. To focus on this dissection we have calculated group increments which give the "base" component of the steric energy for the Schleyer and the Allinger force fields; Table I, footnotes g and i.

In Table II are summarized values for the first members of the alkane series, for many of the relatively strained alkanes for which data are available, and for a few cyclic compounds. It can be seen that strain energy amounts to from 0 to 150% of the steric energy depending upon compound and force field. It further turns out that plots of differences in experimental and calculated strain energies (Δ column of Table II) vs. differences in observed and calculated ΔH_f^0 show rather poor correlations.

Relatively few alkane strain energy values in Tables I and II have been previously reported, and it is for this reason that we included the cyclic compounds. Agreement is relatively good with Allinger strain values based on a different definition,[13] the largest difference being about 0.5 kcal/mol. Differences with the Schleyer definition of strain are larger; some are more than 1.4 kcal/mol.

Differences between "observed" and "raw" calculated strain energies expressed as standard deviations are Franklin (not tabulated), 1.0; Allen (not tabulated), 0.7; Schleyer, 1.0; Allinger, 0.7. These do not parallel the results shown in Figure 2.

Inspection of the "raw" calculated strain energies suggests that some may be biased. One way to express this is to state that the line $y = mx + b$ where y is an unbiased estimate of calculated strain energy for a given value of x, the "raw" calculated strain energy, may not have a slope of 1 and an intercept of 0. We therefore calculated m and b for each case and obtained the following standard deviations for ("observed" strain energy − y): Franklin, 1; Allen 0.4; Schleyer, 0.6; and Allinger, 0.4. Even with this improvement the differences are hardly as striking as those in Figure 2.

Table II. Representative Strain Energies for Alkanes

	Registry no.	ΔH_f[a] exptl	SM[b] corrn	ΔH_f[c] strainless	"Exptl"[d] strain energy	SE[e] MM (Schleyer)	SE[f] strainless (Schleyer)	Strain[g] energy calcd (Schleyer)	Δ[h] (Schleyer)	SE[i] MM (Allinger)	Strainless (Allinger)	Strain[g] energy calcd (Allinger)	Δ[h] (Allinger)
Ethane	74-84-0	−20.24	0.00	−20.00	−0.24	1.04	1.20	−0.16	−0.08	2.37	2.51	−0.14	−0.10
Propane	74-98-6	−24.82	0.00	−25.15	0.33	1.72	1.78	−0.06	0.39	3.08	3.12	−0.04	0.37
Butane	106-97-8	−30.15	0.27	−30.31	−0.11	2.35	2.35	−0.01	0.11	3.71	3.73	−0.02	−0.09
Isobutane	75-28-5	−32.15	0.00	−32.40	+0.25	2.08	2.51	−0.43	0.68	2.10	2.17	−0.07	0.32
Neopentane	463-82-1	−39.67	0.00	−40.54	0.87	2.16	3.05	−0.89	1.76	−0.38	−0.09	−0.29	1.16
2,3-DiMe-C4	79-29-8	−42.49	0.27	−44.80	2.04	6.28	3.81	2.47	−0.43	3.85	1.83	2.02	0.02
2,3-DiMe-C5	565-59-3	−47.62[j]	0.40	−49.95	1.93	8.89	4.38	4.51	−2.58[j]	5.91	2.44	3.47	−1.54[j]
2,4-DiMe-C5	108-08-7	−48.28	0.11	−49.95	1.56	5.66	4.38	1.28	0.28	3.66	2.44	1.22	0.34
2,5-DiMe-C6	592-13-2	−53.21	0.26	−55.11	1.64	6.50	4.95	1.55	0.09	4.69	3.05	1.64	0.00
2,2-DiMe-C6	590-73-8	−53.71	0.38	−56.00	1.91	6.12	4.77	1.35	0.56	3.10	1.75	1.35	0.56
2,2,3-Tri-MeC4	464-06-2	−48.95	0.00	−52.94	3.99	8.68	4.35	4.33	−0.34	3.00	−0.43	3.43	0.56
2,2,4-Tri-MeC5	540-84-1	−53.57	0.03	−58.09	4.49	8.91	4.93	3.98	0.51	4.20	0.18	4.02	0.47
2,2,3-Tri-MeC5	564-02-3	−52.61	0.20	−58.09	5.28	10.92	4.93	5.99	−0.71	4.81	0.18	4.63	0.65
2,2,3,3-Tetra-MeC4	594-82-1	−53.99	0.00	−61.08	7.09	12.41	4.90	7.51	−0.42	3.08	−2.68	5.76	1.33
2-Me3Et-C5	609-26-7	−50.48	0.43	−55.11	4.20	10.84	4.95	5.89	−1.69	7.38	3.05	4.33	−0.13
Cyclopentane	287-92-3	−18.46	0.00	−25.77	7.31	(11.03)	2.87	8.16	−0.85	(11.76)	3.05	8.71	−1.40
Cyclohexane	110-82-7	−29.43	0.00	−30.92	1.49	6.00	3.44	2.56	1.07	5.94	3.66	2.28	−0.79
cis-Decalin	493-01-6	−40.38	0.00	−46.02	5.98	(11.97)	5.98	5.99	−0.35	(8.06)	1.69	6.37	−0.73
trans-Decalin	493-02-7	−43.52	0.00	−46.02	2.45	(9.26)	5.98	3.28	−0.83	(5.48)	1.69	3.79	−1.34
Norbornane[k]	279-23-2	−12.60	0.00	−30.57	17.97	21.23	4.27	16.97	1.01	18.12	−0.14	18.26	−0.29
Adamantane[l]	281-23-2	−32.96	0.00	−40.52	7.56	(14.06)	6.24	7.82	−0.26	(5.00)	−2.72	7.72	−0.16

[a] References 9–11. [b] Statistical mechanical correction, ref 18. [c] Footnote *d*, Table I. [d] Column 5 + column 4 − column 3. [e] Schleyer 1973, ref 12, or Allinger 1971 force field, ref 13. Values in parentheses calculated from Tables II and VI, ref 12. [f] Footnote *g*, Table I. [g] SE(MM) − SE(strainless). [h] "Exptl"—calcd strain energy. [i] Footnote *i*, Table I. [j] Comparison of related compounds suggests that literature ΔH_f^0 (298) is about 0.6 kcal/mol too negative. [k] Reference 20. [l] Reference 21. Other values are −30.65 (ref 22) and −30.57 (ref 23).

Everyone agrees that force fields are going to undergo further refinement, and such refinements may lead to some further improvements of calculated ΔH_f^0 values. However, the larger issue involved in finding data for calibrating the van der Waals terms of force fields remains: there are not enough good ΔH_f^0 data for highly crowded molecules.

We therefore suggest that it may prove useful to adopt a different approach, taking obvious precautions to avoid circular reasoning. We may assume that the Taft E_s values are a generally good measure of steric hindrance, and may then use carefully chosen reaction series for providing additional values of van der Waals strain. This argument is, of course, the exact converse of the one we have used previously.[5,6] Data pertaining to van der Waals forces are even scarcer for compounds other than alkanes, and carefully selected reaction data may provide a valuable additional set of reference values.

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Prototropic Equilibrium of Imines. *N*-Benzylidene Benzylamines

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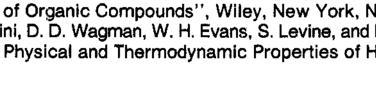
The 1,3-prototropic shift of imines, exemplified in isomerization of unsymmetrically substituted *N*-benzylidene benzylamines, has been reexamined. Equilibrium constants for para-monosubstituted systems were determined by NMR methods; the constants do not show the anomalies reported in older work, and are adequately correlated by the Hammett equation ($\rho = 0.94$).

Recent investigations[1] of prototropic equilibration of nitrones Ia ⇄ Ib (Behrend rearrangement) in this laboratory invited a comparison with the corresponding imines, IIa ⇄ IIb. Imine isomerization had been investigated by Shoppee,[2,3]



$$\begin{array}{ccc} \mathrm{ArCH_2{-}NX} & \rightleftarrows & \mathrm{ArCH{=}NX} \\ \| & & | \\ \mathrm{CHAr'} & & \mathrm{CH_2Ar'} \end{array}$$

Ia, IIa Ib, IIb

Ia, Ib, X = oxygen atom; IIa, IIb, X = electron pair

who brought about equilibration by heating *N*-benzylidene benzylamines with sodium ethoxide solution, over 40 years ago. His results on the effect of substituents, particularly alkyl groups, played a role in the early development of the theory of hyperconjugation.[4] Much later, the mechanism of isomerization was investigated by Cram and Guthrie,[5] who showed that it probably involved formation of a delocalized carbanion, rather than the synchronous process originally proposed.

In the ensuing years, uncertainties developed about the interpretation of the equilibrium constants reported by Shoppee. Baker in 1952 stated that the effects of substituents could not be satisfactorily assessed.[6] The effects of para substituents were not acceptably consistent with the correlations subsequently developed by Hammett, and could not be satisfactorily interpreted according to theories of electronic influences. The equilibrium constant for the *p*-methyl substituent, of particular importance for hyperconjugation in its earliest development, was especially inconsistent.

At the time of Shoppee's investigations, most instrumental methods of analysis had not been developed. As a consequence, he had to use an indirect and error-prone analytical method to determine the composition of the equilibrium mixtures of imines. He hydrolyzed the imines, converted the resulting benzaldehydes to dinitrophenylhydrazones, and compared the melting range of these mixtures with the phase diagram determined from known mixtures. Although this method is in principle sound, its reliability is vitiated if unsuspected traces of a third component should be present; it is also potentially sensitive to variations in yield of the conversion to dinitrophenylhydrazones. It therefore seemed desirable to reinvestigate the subject, not only for comparison with the Behrend rearrangement, but because of the importance of imine tautomerism in synthesis and in biological transamination.

We have prepared a series of para-substituted *N*-benzylidene benzylamines, all of which are known, by warming the corresponding benzaldehydes and benzylamines together. The purified imines consisted of but a single geometrical isomer, insofar as we could determine by infrared and NMR spectroscopy, consistent with Ossorio's report[7] that only the anti isomer is present significantly at equilibrium. We did not include the *p*-nitro substituent, although we would have liked to, because its reaction with sodium ethoxide is more complex (a nitronate salt is apparently formed, and is the basis for a microanalytical determination of benzylamine[8]).

We equilibrated the imines by refluxing them in a 1 M solution of sodium ethoxide in absolute ethanol for periods of 2–36 h. Analysis of the mixtures was accomplished with NMR spectroscopy. Neither the methylene nor the methyne hydrogens of the pairs of tautomers were sufficiently well resolved, unfortunately. However, the methyl signals of the mixtures from the *p*-methyl, *p*-methoxy, and *p*-dimethylamino systems allowed their compositions to be determined. For the *p*-chloro system, hydrolysis of the imines to the corresponding mixture of benzaldehyde and *p*-chlorobenzaldehyde was necessary; the signals of the aldehyde protons were separated by 2.5 Hz.

For each substituent, equilibrium was approached from both sides, and values were determined at a series of times to be sure that equilibrium had been reached. The mean values