C_5H_9D), 70 (<0.1), 69 (0.8), 68 (3.9), 67 (1.5). Comparison to a mass spectrum of 1-pentene-d_0 showed that the product was ≥99.5% d_1.

(17) Dimerization of 2-Deuterio-1-pentene. The procedure was identical with the dimerization of 1-pentene in the comparative rate study; $k = 0.030 \pm 0.003$ min^{-1}. The individual rate constants are 0.022 ± 0.002 (tt dimer) and 0.0085 ± 0.0008 min^{-1} (ht dimer). For undeuterated 1-pentene they are 0.073 ± 0.007 and 0.010 ± 0.00) min^{-1}, respectively. Therefore, for 2-propyl-3-methyl-1-hexene $k_H/k_D = 3.34 \pm 0.67$ and for 2-propyl-1-heptene $k_H/k_D = 1.20 \pm 0.24$.

After 10 h GLC analysis showed that the dimerization was 80% complete. The reaction mixture was passed down a short column of alumina, and the dimers were isolated by preparative GLC.

(a) 2-Propyl-3-deuterio-3-(monodeuteriomethyl)-1-hexene (tt Dimer). ^{1}H NMR ($CDCl_3$): 5.27 (m, 2, $=CH_2$), 7.50–9.63 ppm (m, 16, aliphatic protons). ^{2}H{^{1}H} NMR ($CDCl_3$, ppm upfield of $CDCl_3$): 5.16 (s, 1), 6.25 (s, 1). ^{13}C{^{1}H} NMR ($CDCl_3$, 67.89 MHz): identical with the spectrum of the undeuterated compound except that the singlet at 20.1 ppm is replaced by a triplet at 19.7 ppm ($^1J_{CD}$ = 18.8 Hz), and the singlet at 39.8 ppm is replaced by a triplet at 39.2 ppm ($^1J_{CD}$ = 19.6 Hz). See the preparation of the authentic undeuterated compound and Figure 3 for peak assignments. We estimate from the ^{13}C NMR data that in this sample we could have detected as little as 10% of 2-propyl-3-methyl-1-hexene which was not deuterated in the specified positions.

(b) 2-Propyl-3,4-dideuterio-1-heptene (ht Dimer). ^{1}H NMR ($CDCl_3$): 5.30 (m, 2, $=CH_2$), 7.80–9.50 (m, 16, aliphatic protons). ^{2}H{^{1}H} NMR ($CDCl_3$, ppm upfield of $CDCl_3$): 5.27 (s, 1), 5.83 (s, 1). ^{13}C{^{1}H} NMR ($CDCl_3$): identical with spectrum of the undeuterated compound except that the singlet at 27.7 ppm is replaced by a triplet at 27.2 ppm ($^1J_{CD}$ = 19.3 Hz) and the singlet at 36.1 ppm is replaced by a triplet at 35.7 ppm ($^1J_{CD}$ = 19.1 Hz). See the preparation of the authentic undeuterated compound and Figure 2 for peak assignments. We estimate from the ^{13}C NMR data that in this sample we could have detected as little as 10% of 2-propyl-1-heptene which was not deuterated in the specified positions.

(18) Codimerization of Propylene and 2-Deuterio-1-pentene. (a) Preparation of Authentic Codimers. TaCp″(cyclooctene)Cl_2 (0.159 g, 0.32 mmol) was suspended in 4 mL of pentane into a glass pressure bottle and stirred under 40 psi propylene at 50 °C until a yellow-orange solution formed. Then 1 mL of 1-pentene was added by syringe, followed by another after 5 h. Samples for GLC analysis were withdrawn within the first hour. For 2-isopropyl-1-pentene (isomer A, Figure 4), $k_H(A) = 4.1$ and 4.2 in two different runs; for 2,3-dimethyl-1-hexene (isomer B, Figure 4), $k_H(B) = 2.0$ and 2.3 in two different runs. After 28 h the solution was passed down a short column filled with alumina and distilled by using a short Vigreux column to eliminate most of the solvent and 2,3-dimethyl-1-butene. The mixture of the two major C_8 codimers was isolated by preparative GLC and examined by ^{13}C NMR; chemical shifts and assignments are shown in Figure 4. Authentic samples were prepared by a Wittig reaction from the two commercially available ketones. They were identical in all respects with the products of the catalytic reaction. (The units of k are 10^{-2} min^{-1}.)

(b) Preparation of Labeled Codimers. Catalytic reactions identical with the above using 2-deuterio-1-pentene gave A and B with $k_D(A)$ = 4.2 and 3.9 and $k_D(B)$ = 0.66 and 0.70. Therefore $k_H/k_D = 1.0$ for A and $k_H/k_D = 3.2$ for B. The mixture of A and B was isolated by preparative GLC and examined by ^{13}C NMR at 67.89 MHz (Figure 4). Approximately 5% of authentic all-protio A (prepared from the ketone) was added to confirm that the peak at δ 33.843 was due to the A4 carbon atom with a proton attached. By comparing the two peak areas we could show that the codimer A was labeled to the extent of 97–98% as shown. (The units of k are 10^{-2} min^{-1}.)

Acknowledgments. We thank the National Science Foundation for support (CHE 79 05307), the Francis S. Bitter National Magnet Laboratory for use of their high-field NMR facilities, and Professor G. M. Whitesides for use of his GC/mass spectrometer.

Steric Effects. A Study of a Rationally Designed System

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New South Wales 2006, Australia. Received February 8, 1980

Abstract: The principles for the rational design of systems suitable for the study of steric effects are defined. A suitable *molecular framework* [6-(2-X-phenyl)-5-Y-1,1-dimethylindan, **1**] was synthesized and a study of internal rotation by dynamic NMR spectroscopy (DNMR) of 33 derivatives, differing principally in the nature of the *molecular fragment* (X), showed the following. (i) For **1** (Y = Me; X = halogen) the rotational barriers ($\Delta G^{\ddagger}$) increase smoothly and monotonically with the van der Waals radius of X (r_x), which permits the estimation of *effective* r_x for fragments of lower symmetry. (ii) The rotational barriers are the sum of additive contributions, designated *interference values* (I^{H-X}), which can be used to predict the rotational barriers in 2,2′-disubstituted biphenyls. (iii) A simple geometrical parameter, apparent overlap (r^*), which is related to the distortion of the framework in the transition state, is proposed and found to have an excellent linear correlation with the barrier to rotation in 2,2′-disubstituted biphenyls. (iv) This correlation can be used for a semiquantitative estimation of rotational barriers in biaryls and other systems.

Steric hindrance can be defined as the energy penalty associated with crowding of nonbonded molecular fragments. The study of this phenomenon must therefore involve notions of size (typically defined in terms of van der Waals radii[1]) of the fragments, the geometry of the systems within which they interact, and the energy associated with the interaction(s). Steric hindrance forms a persistent theme in chemistry and has been invoked to rationalize innumerable observations. It is amenable to theoretical treatments,[2] but *systematic* experimental studies are relatively few with most of the recent work being summarized by Charton,[3] who has established statistically significant correlations between the size of molecular fragments and the energetics of a number of processes reported by other workers. Steric interactions have also been recently critically reviewed by Förster and Vögtle.[4]

We decided to approach the problem by designing a system whose energetics would shed light on the relationship between the

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(2) N. L. Allinger, *Adv. Phys. Org. Chem.*, **13**, 1 (1976).

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size of the molecular fragments, the *geometry* of nonbonded interactions, and the *energy penalty* involved. Thus, if Charton's work could be described as an attack on the problem by statistics, ours amounts to molecular engineering.

Rational Design of a System for the Study of Steric Hindrance. This can be subdivided into a number of requirements, most of which can be only approximated in practice:

(1) The process chosen for study should be intramolecular, e.g., a conformational change, because the geometry of intermolecular processes is more difficult to define. This requirement implies the design of a *moleular framework*.

(2) Steric effects should clearly be dominant and, to make them larger than the unavoidable contributions from electronic effects, hydrogen bonding, solvent effects, etc.,[5] they must be large in absolute terms. It follows that processes with small energy changes are inherently unsuitable and this in practice excludes the study of equilibria due to obvious analytical difficulties. The failure to meet this requirement is probably a contributory cause for the poor correlation between the *G* values derived from equilibria in monosubstituted cyclohexanes[6] and the van der Waals radii of the substituents.

(3) The system must be accessible to kinetic study for a wide range of *molecular* fragments (typically functional groups) attached to the basic molecular framework. A special problem is associated with entropy considerations. Ideally, precise values of $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ are desirable, but in practice often only the free energy is conveniently accessible. For this reason, the minimum requirement is for the series studied to be isoentropic.

(4) The potential-energy profile associated with the conformatinal process must be well defined; i.e., it should be possible to determine the change of geometry associated with the energy change corresponding to the barrier. The requirement of large barriers also implies steep energy wells and hence justifies disregarding the population in higher vibrational states.

The lack of well-defined geometry in some systems which otherwise comply with the above requirements[7,8] limits the generality of these results.

(5) It is highly desirable for either the ground state or the transition state to be insensitive to the size of the molecular fragments. This facilitates the analysis of data for a series of compounds because all members of the series have a common reference point. If this condition is not met, the barrier will reflect the difference between steric interactions in two environments which may be of different sensitivity to steric hindrance. For this reason *G* values,[5] *P* values,[9] and other processes[10] related to rotation about sp^3–sp^3 carbon–carbon bonds are not ideal with respect to molecular framework: there are significant gauche interactions in the ground state.

(6) The molecular framework must be capable of accommodating a large number of molecular fragments while remaining unchanged, in particular with respect to the type of energy profile and electronic effects.

(7) Limitations associated with the anisotropy of size[1] of the molecular fragments must be taken into consideration. Thus hydrogen and the halogens form a particularly well-defined series and should be of special value as reference points.

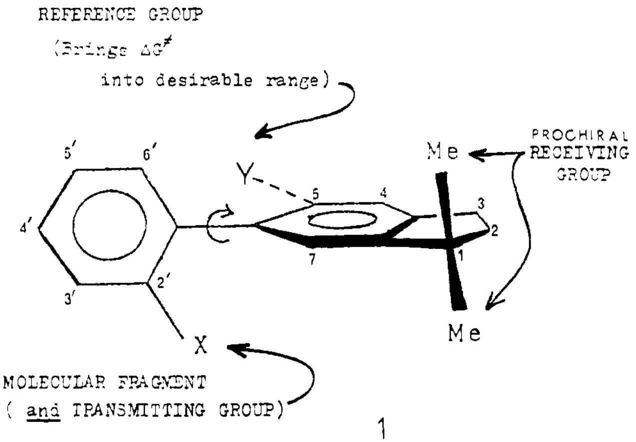

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Figure 1. A rationally designed molecular framework for the study of steric interactions.

(8) The series of compounds consisting of the molecular framework with various molecular fragments must be synthetically accessible.

It will be noted that specifications (3) and (8) are purely operational criteria, but the remaining six are of fundamental significance. Some of the points made here (e.g., the anisotropy of van der Waals surface[9] and the isoentropy problem[7]) have been made before, while Förster and Vögtle have independently proposed similar arguments in a recent review,[4] but to our knowledge the analysis presented above has not been utilized to *design* systems for systematic investigation of nonbonded interactions.

The system chosen in this work (Figure 1) is based on a 2,2′-disubstituted biphenyl skeleton and is, therefore, expected to exist in a conformation with the benzene rings essentially orthogonal in the ground state, although the actual situation is more complex.[11,12] The basic assumptions made in our work are that the steric repulsions between the fragments X and Y and the hydrogen atoms on the other benzene ring, in the coplanar transition state, are the decisive factors determing the size of the barrier to rotation in **1**, but that the interactions between the fragments X and Y and the π clouds of the second benzene ring in the ground state are very much less severe and can be neglected for all but the largest molecular fragments. This second assumption, which makes system **1** conform to the requirement (5) above, is based only on the examination of models and must be tested empirically.

The barriers to internal rotation in biphenyl derivatives have been the subject of numerous classical studies[13] but as these relied almost entirely on racemization rates the requirement of very large barriers severely limited the range of molecular fragments whose interactions could be investigated. A number of workers utilized DNMR techiques[14] for this purpose,[15,16] but in all cases a prochiral group (generally $-CHMe_2$ or $-CH_2X$) was placed at C-2 (and/or C-2′) of the biphenyl skeleton as a probe for the dynamic process, thus necessarily involving the steric interactions of a highly anisotropic group in the process. System **1** can be considered as a modification with the prochiral group removed from the site of the steric interaction and made more efficient by incorporating it into a cyclic fragment.

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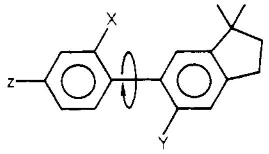
Table I. Activation Parameters for 6-(2-X-4-Z-Phenyl)-5-Y-1,1-dimethylindans



	Y	X	Z	temp range, K	$\Delta G^\ddagger_m$,[a] kJ mol^{-1}	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J mol^{-1} K^{-1}	$\Delta G^\ddagger_{340}$,[b] kJ mol^{-1}	$\Delta G^\ddagger_{340}$,[c] kJ mol^{-1}
1	CH_3	I	H	356-415	89.9 ± 0.7	55.7 ± 1.3	−88 ± 3.5	85.8 ± 1.0	86.3 ± 1.8
2	OCH_3	I	H	299-325	69.8 ± 0.6	55.4 ± 1.5	−46 ± 5	71.1 ± 0.7	72.0 ± 1.3
3	CH_3	Br	H	335-367	83.8 ± 1.1	66.2 ± 1.5	−50 ± 4	83.3 ± 1.2	82.9 ± 1.4
4	CH_3	Cl	H	308-362	78.1 ± 1.0	49.4 ± 0.9	−86 ± 2.5	78.6 ± 1.0	78.5 ± 1.1
5	CH_3	F	H	210-273	51.8 ± 0.6	22.9 ± 2.0	−120 ± 2	63.6 ± 0.8	59.6 ± 3.0
6	CH_3	CH_3	H	337-350	81.2 ± 1.0				80.9 ± 1.0
7	OCH_3	CH_3	H	258-308	62.3 ± 0.7	39.6 ± 0.4	−80 ± 1.5	66.8 ± 0.7	66.8 ± 2.1
8	CH_3	OCH_3	H	259-281	61.4 ± 0.7	48.0 ± 5.5	−50 ± 5.5	64.9 ± 1.0	66.9 ± 2.4
9	CH_3	OH	H	256-269	61.4 ± 0.8				67.5 ± 2.7
10	CH_3	OAc	H	275-290	65.3 ± 0.7	44.1 ± 1.5	−75 ± 5	69.6 ± 1.0	69.8 ± 2.1
11	CH_3	COOMe	H	297-322	70.8 ± 0.7	52.8 ± 0.9	−58 ± 3	72.6 ± 0.7	73.2 ± 1.5
12	OCH_3	COOMe	H	237-273	55.6 ± 0.5	37.2 ± 0.6	−73 ± 2	61.8 ± 0.7	62.3 ± 2.5
13	CH_3	$COCH_3$	H	273,277	64.9 ± 0.7				70.0 ± 2.3
14	CH_3	Ph	H	293-311	70.5 ± 0.7	40.6 ± 1.5	−99 ± 5	74.2 ± 0.9	73.5 ± 1.6
15	CH_3	CH_2OH	H	336-364	82.4 ± 0.9	64.0 ± 1.4	−53 ± 4	81.9 ± 0.9	81.6 ± 1.2
16	CH_3	CH_2OAc	H	333-404	84.6 ± 0.9	67.3 ± 1.0	−47 ± 2.5	83.2 ± 1.0	82.4 ± 1.6
17	CH_3	$CH(CH_3)_2$	H	420-457	100.8 ± 0.7	51.5 ± 2.1	−113 ± 5	89.7 ± 1.9	93.0 ± 3.0
18	CH_3	CF_3	H	392-422	97.3 ± 1.1	77.8 ± 3.7	−48 ± 9	94.1 ± 1.7	92.0 ± 2.7
19	OCH_3	CF_3	H	307-332	74.3 ± 0.8	57.0 ± 1.7	−53 ± 5	75.4 ± 0.9	75.9 ± 1.3
20	CH_3	NO_2	H	275-304	68.8 ± 1.0				72.8 ± 2.2
21	OCH_3	NO_2	H	233-253	55.3 ± 0.6				63.0 ± 3.0
22	CH_3	NH_2	H	323-361	80.8 ± 0.9	53.1 ± 1.3	−81 ± 4	80.7 ± 0.9	80.6 ± 1.0
23	CH_3	$NHCH_3$	H	352-376	86.6 ± 0.8	52.7 ± 3.3	−93 ± 10	84.4 ± 1.1	84.7 ± 1.4
24	CH_3	$N(CH_3)_2$	H	301-338	71.5 ± 0.6	44.5 ± 1.0	−84 ± 3	73.2 ± 0.7	73.1 ± 1.1
25	CH_3	$N(CH_3)_3^+$	H	>422					>94
26	CH_3	$NHCOCH_3$	H	284-308	67.6 ± 0.6	42.6 ± 0.3	−84 ± 1	71.3 ± 0.7	71.1 ± 1.7
27	CH_3	$Si(CH_3)_3$	H	366-427	92.1 ± 0.8	53.6 ± 1.3	−97 ± 3.5	86.6 ± 1.0	87.6 ± 2.2
28	CH_3	SH	H	333-349	81.2 ± 0.9	45.9 ± 1.6	−103 ± 5	81.1 ± 0.9	81.1 ± 0.9
29	CH_3	SCH_3	H	337-356	82.2 ± 0.8	53.1 ± 1.2	−84 ± 3.5	81.6 ± 0.9	81.7 ± 1.0
30	CH_3	CN	H	244-254	58.8 ± 0.8				66.0 ± 3.0
31	CH_3	HgCl	H	320-351	73.7 ± 0.5	39.9 ± 1.6	−102 ± 5	74.6 ± 0.5	74.1 ± 0.6
32	CH_3	Cl	NO_2	310-344	76.5 ± 0.9	56.2 ± 0.9	−62 ± 3	77.3 ± 0.9	77.5 ± 1.2
33	CH_3	F	NO_2	213-243	48.6 ± 0.6	19.6 ± 0.8	−127 ± 3.5	62.9 ± 0.9	57.4 ± 3.3

[a] $\Delta G^\ddagger$ at the temperature at the center of the range over which kinetic data was obtained. [b] $\Delta G^\ddagger$ at 340 K, calculated using $\Delta G^\ddagger_m$ and $\Delta S^\ddagger$. [c] $\Delta G^\ddagger$ at 340 K, calculated using $\Delta G^\ddagger_m$ and $\Delta S^\ddagger_{av}$.

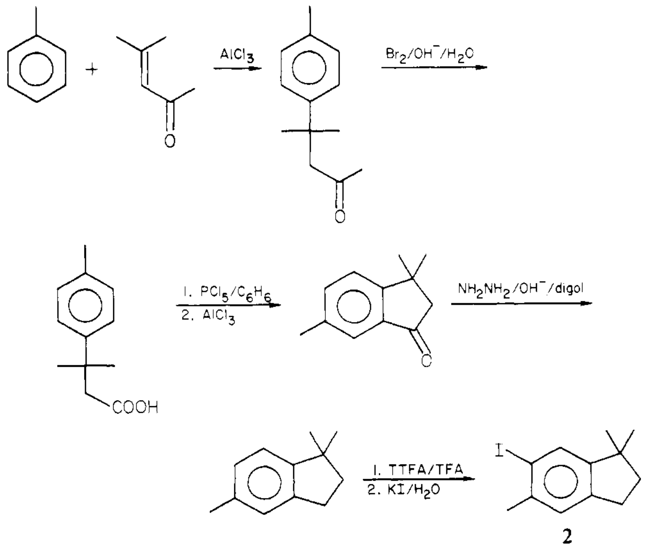
While an electronic factor is clearly involved in the rotational barrier in series **1** because the planar transition state is stabilized by conjugation, the effect is expected to be insensitive to substituents (X and Y) as even extreme cases of through conjugation in biphenyls are associated with only minor changes in the energy barrier.[16] The essential skeleton of the system **1** (i.e., the 1,1-dimethylindan ring, usually with X = Me) contains no substituents with pronounced conjugative effects and some results obtained in the course of this work (see below) confirm that the series can be considered uniform as far as electronic effects are concerned.

The key intermediate (**2**) in the synthesis of the series **1** (Y = Me), which forms the bulk of this study (28 compounds), was conveniently prepared via the sequence outlined in Scheme I. The corresponding intermediate (**3**) used for the preparation of the series **1** (Y = OMe) was prepared via the sequence outlined in Scheme II. The elaboration of these intermediates to the biphenyl derivatives via the Ullman reaction and other synthetic procedures are given in the Experimental Section.

Activation parameters were obtained by straightforward DNMR procedures[14] using line-shape analysis[17] and the data are summarized in Table I. An account of the procedure is given in the Experimental Section, but two points need emphasis:

(i) Although DNMR is notoriously unsuitable for accurate determination of $\Delta S^\ddagger$, we have some evidence for the series being essentially isoentropic. The plot (Figure 2) of $\Delta G^\ddagger$ for the halogen derivatives against temperature consists of four nearly parallel lines. Further, the values of $\Delta G^\ddagger_{340}$ (the free energy of activation at 340 K, the mean temperature for the whole series) obtained by using individual values of $\Delta S^\ddagger$ are very close (Table I) to those obtained by using the average entropy of activation for the series

Scheme I



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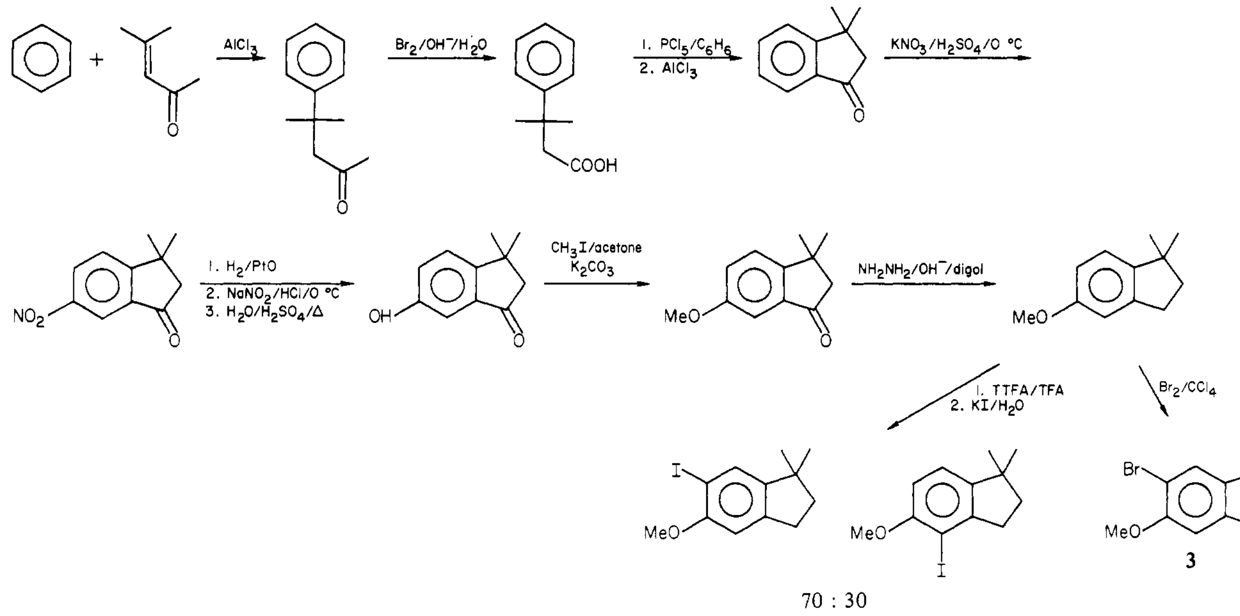
Scheme II



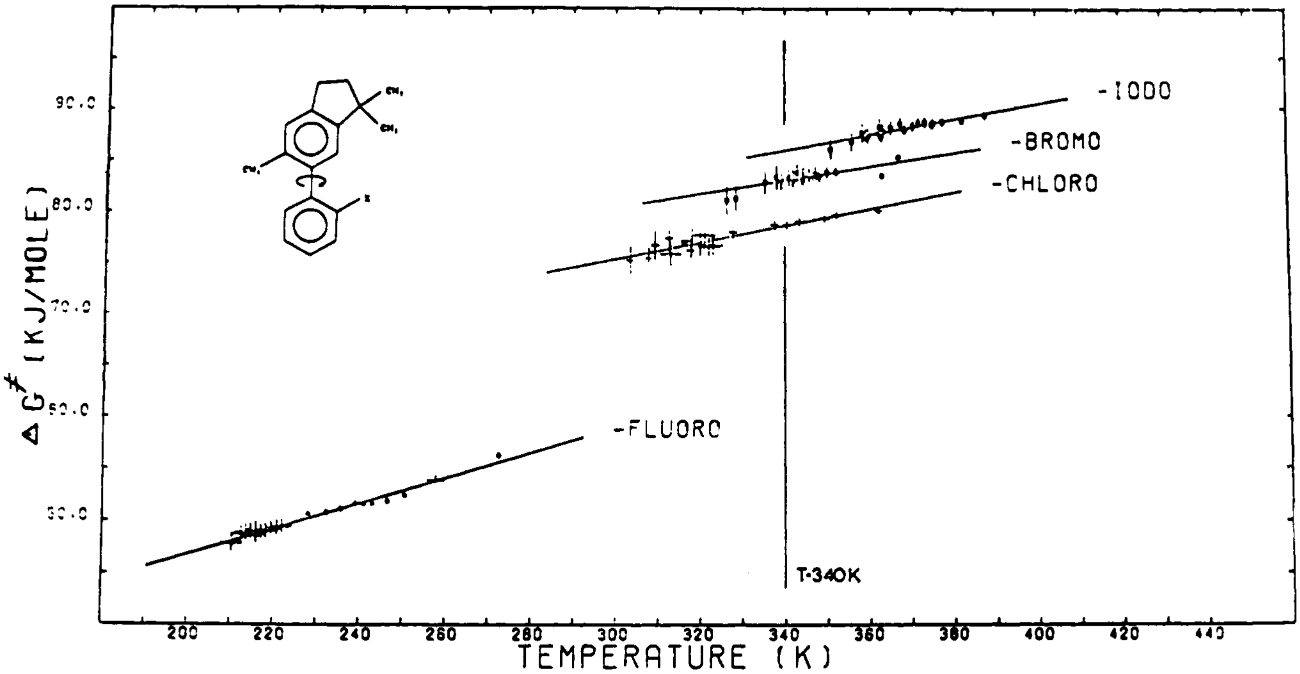


Figure 2. Plot of $\Delta G^{\ddagger}$ against temperature for the 6-(2-X-phenyl)-1,1,5-trimethylindans, where X = halogen.

($\Delta S^{\ddagger}_{av} = -79 \pm 28$ J mol^{-1} K^{-1}). The entropy of activation is thus small and negative and, even if the system is not perfectly isoentropic, the errors due to this approximation (reflected in the confidence limits) are not very large and are further reduced by minimizing the entropy correction by the arbitrary choice of the mean temperature of 340 K.

The system **1** thus meets the operational criteria called for above.

(ii) The data in Table I were obtained from the examination of variable temperature NMR spectra taken in a range of solvents (carbon disulfide, toluene-d_8, dimethyl-d_6 sulfoxide, dioxane-d_8, hexachlorobutadiene, methanol-d_4, deuteriochloroform, and acetone-d_6). Typically, different solvents produced different values of $\Delta\nu_s$ (the chemical-shift differences between the resonances of the exchanging groups at slow exchange limit) which, together with the use of spectrometers operating at different magnetic fields, permitted us to extend the temperature range. Generally, each substance was examined in more than one solvent and, for all cases studied, any solvent effect on the measured rate constants was less than the scatter of the data about the least-squares line of best fit in the Arrhenius plots. Thus for all cases examined solvent interactions have a negligible effect on the magnitude of the rotational barrier, in agreement with the absence of significant solvent effects on the rates of racemization of biphenyl derivatives.[18]

Discussion of Results

The Relation between the Barrier to Rotation and the Size of the Molecular Fragment X. A plot of the energies of activation ($\Delta G^{\ddagger}_{340}$) for the halogen derivatives in the series **1** (Y = Me; X = F, Cl, Br, I; Table I) against their van der Waals radii[1] forms a smooth monotonic curve (Figure 3). The values of $\Delta G^{\ddagger}_{340}$ for **1** (Y = Me; X = OMe, SMe, and SiMe$_3$) (examination of models reveals that silicon is the interacting surface) fall exactly on this curve when plotted against the van der Waals radii[1] of oxygen,

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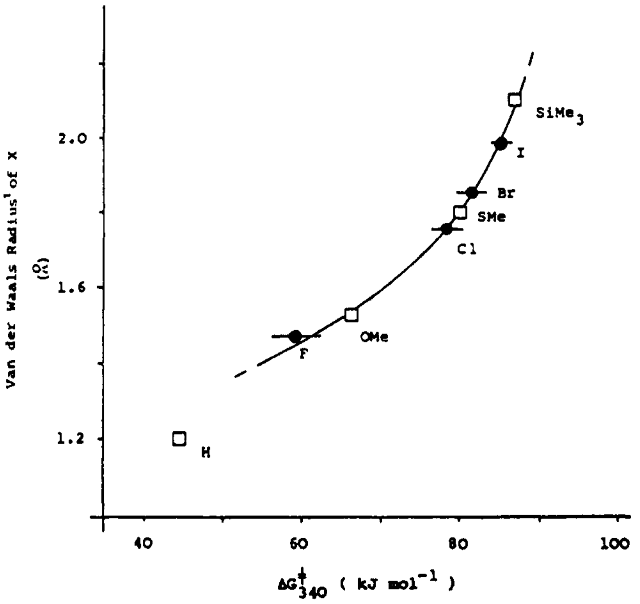

Figure 3. Plot of $\Delta G_{340}^{\ddagger}$ against the van der Waals radius[1] of X in some 6-(2-X-phenyl)-1,1,5-trimethylindans (**1**, Y = Me).

sulfur, and silicon, respectively (Figure 3). The value of $\Delta G^{\ddagger}_{340}$ for **1** (Y = Me; X = H) can only be derived indirectly (see below), but it can be seen that it also conforms with the monotonic relationship shown in Figure 3. The series **1** (Y = Me) thus exhibits a very significant correlation between the size of the molecular fragment involved in a steric interaction and the magnitude of the barrier which arises from this interaction. The effective van der Waals radii (i.e., the apparent size in the context of this particular interaction) of less symmetrical groups were then obtained by algebraic intrapolation of the remaining activation parameters (Table I) to the curve in Figure 3, to give the results shown in Table II.

It can be seen that, whenever comparison could be made with either van der Waals radii derived from crystallographic data[1] or with effective sizes obtained by Charton,[3] our results appear reasonable. A conspicuous exception is the results for X = NH_2 and NHMe, which appear "larger" than NMe_2. The latter has an effective radius (1.61 Å) close to the van der Waals radius of nitrogen (1.56 Å)[1] and we rationalize these results by invoking nonsteric (e.g., conjugative, charge transfer, or hydrogen bending) intramolecular effects, which will be the subject of further study.

The system **1** (Y = Me) thus offers a convenient method for obtaining effective sizes of molecular fragments, which appear to be comparable with data obtained by other methods.[1,3] Particularly interesting are the results for the methyl and trifluoromethyl groups, which are close to Charton's minimum sizes,[3] thus providing evidence for the cog-wheeling effect.[7,19] Data for fragments where the point of attachment is an sp^2-hybridized carbon atom (**1**, Y = Me; X = COOMe, COMe, Ph; Table II) fall into a narrow range of 1.56–1.62 Å which presumably represents the effective thickness of this atom. Similarly, sp^2-hybridized nitrogen (**1**, Y = Me; X = NHCOMe, NO_2) appears to be approximately 1.6 Å thick. Attention is also drawn to the result for mercury since crystallographic data suitable for the estimation of van der Waals radii of covalently bound metals are rare.[1]

Table II. Effective van der Waals Radii (Å) Derived from Rotational Barriers in 6-Aryl-1,1,5-trimethylindans (**1**, Y = Me)

X	effective radius (this work)[a]	van der Waals radius (Bondi)[1]	effective radius (Charton)[3]
I	1.97 ± 0.06	1.98	1.97
Br	1.86 ± 0.04	1.85	1.85
Cl	1.73 ± 0.03	1.75	1.73
F	1.47 ± 0.01	1.47	1.47
OMe	1.52 ± 0.03	1.52 (O)	1.56
OH	1.53 ± 0.03		1.52
OAc	1.56 ± 0.03		
SMe	1.82 ± 0.03	1.80 (S)	1.84
SH	1.80 ± 0.03		1.80
CH_3	1.80 ± 0.03	2.0	1.72, 2.23[b]
CF_3	2.2 ± 0.13		2.11, 2.74[b]
CH_2OH	1.82 ± 0.04		1.73
CH_2OAc	1.84 ± 0.05		
$CH(CH_3)_2$	2.2 ± 0.12		1.96
t-Bu	3.6 ± 0.5[c]		2.4, 3.2[b]
COOMe	1.62 ± 0.03		
$COCH_3$	1.56 ± 0.04		
Ph	1.62 ± 0.03	1.77	1.77
CN	1.51 ± 0.03	1.78	1.60
NMe_2	1.61 ± 0.02	1.55 (N)	1.63
NHMe	1.91 ± 0.05		
NH_2	1.79 ± 0.03		
NMe_3^+	>2.27		2.42, 3.11[b]
$NCOCH_3$	1.58 ± 0.03		
NO_2	1.61 ± 0.04		1.79
HgCl	1.63 ± 0.01	1.5–1.65 (Hg)	
$SiMe_3$	2.01 ± 0.08	2.1	2.6, 3.99[b]

[a] Derived by intrapolation (see Figure 3, Table I, and text). Confidence limits reflect those of the activation parameters (Table I). [b] Charton's value of $r_{\min}$ and $r_{\max}$. [c] See text. The $\Delta G^{\ddagger}{}_{340}$ for this compound is well beyond the range encompassed by the halogens so the effective radius of *tert*-butyl is not well defined.

Table III. I_{340}^{X-H} Values for the Rotational Barriers of Biphenyls

interacting group (X or Y)	I_{340}^{X-H}, kJ mol^{-1}	interacting group (X or Y)	I_{340}^{X-H}, kJ mol^{-1}
I	45.7 ± 2.7	$CH(CH_3)_2$	52.6 ± 4.1
Br	42.5 ± 2.5	*t*-Bu	76.6 ± 4.3[a]
Cl	38.1 ± 2.2	COOMe	34.3 ± 3.1
F	19.2 ± 4.1	$COCH_3$	29.6 ± 3.4
H	~4[a]	Ph	33.1 ± 2.7
MeO	26.6 ± 1.2	CN	25.6 ± 4.1
HO	27.1 ± 3.8	NMe_2	32.7 ± 2.2
AcO	29.4 ± 3.2	NHMe	44.3 ± 2.5
SMe	41.3 ± 2.1	NH_2	40.2 ± 2.1
SH	40.7 ± 2.0	NMe_3^+	>53.6
CH_3	40.4 ± 1.1	$NCOCH_3$	30.7 ± 2.8
CF_3	50.6 ± 3.1	NO_2	32.4 ± 3.3
CH_2OH	41.2 ± 2.3	HgCl	33.7 ± 1.7
CH_2OAc	42.0 ± 2.7	$SiMe_3$	47.2 ± 3.3

[a] See text.

Additivity of Pairwise Contributions and Prediction of Rotational Barriers in Derivatives of Biphenyl. Additivity amounts to the assumption that each of the rotational barriers determined in the system **1** consists of two additive components (I_{340}^{Y-H} and I_{340}^{X-H}) corresponding to interference values due to interactions of fragments Y and X with the hydrogen atoms on the other ring. It is further assumed that it is immaterial which ring carries which fragment; e.g., entries 7 and 8 in Table I should give identical barriers, which is indeed the case. Simple algebraic manipulation shows that certain sets of three barriers will yield sets of three interference values; e.g., entries 7, 11, and 12 in Table I will yield I_{340}^{Me-H}, $I_{340}^{COOMe-H}$, and I_{340}^{OMe-H}. Inspection of Table I reveals that some I_{340}^{X-H} values can be calculated from several sets of independent results, thus affording a test of the assumption of additivity. Thus the particularly important value of I_{340}^{Me-H} has a sevenfold redundancy and the value of I_{340}^{OMe-H} a sixfold redundancy. The values obtained fall into narrow ranges (38.9–41.5 and 25.4–28.0 kJ mol^{-1}, respectively), indicating that the assumption of additivity is substantially obeyed. Average values were used and the errors quoted in Table III reflect the spread of values.

The values listed in Table III were derived in this manner from the free energies of activation listed in the last column of Table I, except for the value of I_{340}^{H-H}, which is simply half of the barrier

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Table IV. Reported and Predicted Activation Parameters for Internal Rotation in Biphenyls

biphenyl substituents				temp,[a] K	$\Delta G^{\ddagger}_{\text{inv}}$,[b] kJ mol^{-1}	$\Delta S^{\ddagger}_{\text{inv}}$,[b] J mol^{-1} K^{-1}	$\Delta G^{\ddagger}_{340}$,[c] kJ mol^{-1}	$\Delta G^{\ddagger}_{340}$(av),[d] kJ mol^{-1}	predicted $\Delta G^{\ddagger}_{340}$,[f] kJ mol^{-1}	ref
2	2′	4	4′							
CH_3	CH_3	H	H	240	72	−48.5 ± 7.5	77.6 ± 1	80	80.8 ± 2	23
I	I	H	H	307	97	−40	99	100	91.4 ± 5	24
MeO	*i*-Pr	H	H	359	80.3 ± 0.3			78.8 ± 0.7	79.2 ± 5	16
i-Pr	*i*-Pr	H	H	>473	>110			>100	105.2 ± 8	15b
I	I	*e*	*e*	298	90–98	−22 to −40	91–100	93–102	91.4 ± 5	24
CF_3	CF_3	NH_2	NH_2	312	101	−70	103	103	101.2 ± 6	25
Br	Br	COOH	COOH	278	84.8	−28	86.4	90	85.0 ± 5	26
t-Bu	NO_2	H	H	336	108	−13	108	108 ± 1	*g*	21
t-Bu	COOH	H	H	341	107	−26	107	107 ± 1	*g*	22

[a] The temperature at the center of the range for the reported data. [b] Data for the *inversion* process at the temperature stated[a] derived from E_a and A (reported). [c] $\Delta G^{\ddagger}$ at 340 K derived from E_a and A (reported). [d] $\Delta G^{\ddagger}$ at 340 K derived using $\Delta S^{\ddagger}_{\text{av}}$ (−79 ± 28 J mol^{-1} K^{-1}). [e] The range of barriers quoted encompasses the results for compounds where both substituents at positions 4 and 4′ were COOMe, COOH, COO^-, NH_2, NH_3^+, and NHCOMe. [f] Using I_{340}^{X-H} values from Table III. [g] See Table III and text.

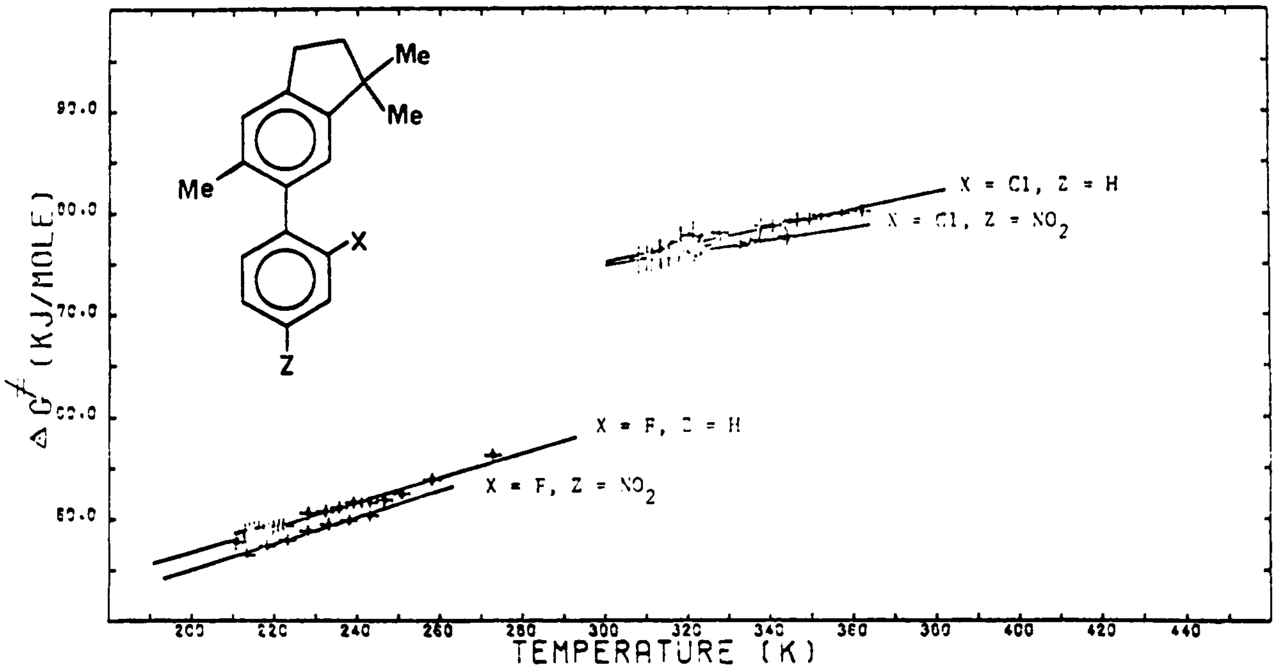
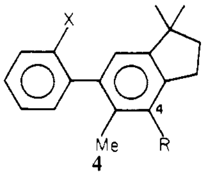


Figure 4. Plot of $\Delta G^{\ddagger}$ against temperature for 6-(2-chloro-4-nitrophenyl)-1,1,5-trimethylindan, 6-(2-fluoro-4-nitrophenyl)-1,1,5-trimethylindan, and the corresponding nonnitrated compounds.

to rotation in biphenyl itself[20] corrected to 340 K, using $\Delta S_{\text{av}}^{\ddagger}$ (see above) and the value of $I_{340}^{t\text{-Bu-H}}$, which is derived from published data[21,22] for 2-nitro-2′-substituted biphenyls, *assuming* additivity, i.e., subtracting our I_{340}^{X-H} values for the appropriate substituent at C-2′ and using the temperature correction based on our $\Delta S_{\text{av}}^{\ddagger}$.

If certain assumptions stated above hold, i.e., (i) the assumption of additivity is indeed correct, (ii) electronic and solvent effects are negligible, and (iii) the effect of the 1,1-dimethylcyclopentene ring in system **1** can be neglected, it should be possible to predict the rotational barrier in any 2,2′-disubstituted biphenyl from the interference values listed in Table III. It can be seen from Table IV that the interference values (I_{340}^{X-H}) have, in fact, a very high predictive capacity for all seven sets of appropriate data which we were able to locate in the literature. These data are confined to 2,2′-disubstituted biphenyls lacking substituents at C-3 and/or C-3′, so as to avoid the consequences of the well-established[27] buttressing effect (see also below).

Table V. Rotational Barriers for Some 6-(2-X-Phenyl)-1,1,5-trimethylindans and Their 4-Bromo Derivatives



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X	R	$\Delta G^{\ddagger}_{340}$,[a] kJ mol^{-1}	$\Delta G^{\ddagger}_{340}$,[b] kJ mol^{-1}
F	H	59.6 ± 3.0	
F	Br	67.9 ± 2.3	8.3 ± 5.3
Cl	H	78.5 ± 1.1	
Cl	Br	87.7 ± 1.9	9.2 ± 3.0
NO_2	H	72.8 ± 2.2	
NO_2	Br	81.2 ± 1.2	8.4 ± 3.4

[a] Calculated using $\Delta S^{\ddagger}_{\text{av}}$ (=−79 J mol^{-1} K^{-1}). [b] The difference between $\Delta G^{\ddagger}_{340}$ values for the compounds with and without bromine at C-4.

Electronic and Buttressing Effects in Biphenyls. Electronic

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(24) C. Cheung King Ling and M. M. Harris, *J. Chem. Soc.*, 1825 (1964).
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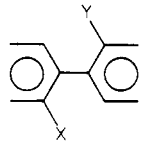
Table VI. Values of Σr^* and $\Delta G^{\ddagger}_{340}$ for 2,2′-Substituted Biphenyls



ref	X	Y	$r_{W(X)}$,[a] Å	$r_{W(Y)}$,[a] Å	Σr^*,[c] Å	$\Delta G^{\ddagger}_{340}$,[b] kJ mol^{-1}
this work	CH_3	*i*-Pr	1.80	2.2	3.3	93.0 ± 3.0
this work	CH_3	*Si*(Me)$_3$	1.80	2.1	3.19	87.6 ± 2.2
this work	CH_3	CF_3	1.80	2.2	3.18	92.0 ± 2.7
this work	CH_3	I	1.80	1.97	3.07	86.3 ± 1.8
this work	CH_3	Br	1.80	1.86	2.95	82.9 ± 1.4
this work	CH_3	*S*Me	1.80	1.82	2.91	81.7 ± 1.0
this work	CH_3	CH_3	1.80	1.80	2.90	80.9 ± 1.0
this work	CH_3	*S*H	1.80	1.80	2.89	81.1 ± 0.9
this work	*O*Me	CF_3	1.52	2.2	2.82	74.9 ± 1.3
this work	CH_3	Cl	1.80	1.73	2.81	78.5 ± 1.1
this work	*O*Me	I	1.52	1.97	2.66	72.0 ± 1.3
this work	CH_3	*C*OOMe	1.80	1.61	2.63	73.2 ± 1.5
this work	CH_3	Ph	1.80	1.62	2.60	73.5 ± 1.6
this work	CH_3	*N*O$_2$	1.80	1.59	2.60	72.8 ± 2.2
this work	CH_3	*C*OCH$_3$	1.80	1.57	2.59	70.0 ± 2.3
this work	CH_3	*O*Me	1.80	1.52	2.49	66.9 ± 2.4
this work	*O*Me	CH_3	1.52	1.80	2.49	66.8 ± 2.1
this work	CH_3	*O*H	1.80	1.52	2.49	67.5 ± 2.7
this work	CH_3	*O*Ac	1.80	1.52	2.49	69.8 ± 2.1
this work	CH_3	F	1.80	1.48	2.43	59.6 ± 3.0
this work	*O*CH$_3$	*C*OOMe	1.80	1.57	2.22	62.3 ± 2.5
this work	*O*CH$_3$	*N*O$_2$	1.52	1.59	2.19	63.0 ± 3.0
23	CH_3	CH_3	1.80	1.80	2.90	80
24	I	I	1.97	1.97	3.24	97 ± 5
25	CF_3	CF_3	2.2	2.2	3.56	103
26	Br	Br	1.86	1.86	3.00	90
16	*O*CH$_3$	*i*-Pr	1.52	2.2	2.89	78.8 ± 0.7
15b	*i*-Pr	*i*-Pr	2.2	2.2	3.7	>100
21	*t*-Bu	*N*O$_2$	3.6 ± 0.5	1.59	4.39 ± 0.5	108 ± 1

[a] From Table II. Values quoted typically have errors of 0.03–0.04 Å which gives r^* an uncertainty no greater than ±0.1 Å. [b] From Tables I and IV (using $\Delta S^{\ddagger}_{av}$). [c] r^* was calculated for the interaction with the atom italicized.

effects due to substituents in system **1** were expected to be negligible by analogy with published[16] data (see above), but further confirmation was sought by incorporating nitro groups at C-4′ of the molecular framework. Comparison of the pairs of entries 4 and 32 as well as 5 and 33 in Table I shows that the differences in the free energies of activation between the pairs are well within the limits of experimental error. Nevertheless, the trends are in the expected direction (i.e., the nitro groups lower the barriers by stabilizing the planar transition states) and this is confirmed by a more detailed examination of the kinetic data (Figure 4).

The influence of buttressing, i.e., of placing a substituent in the proximity of the stericaly interacting fragment, has been established by the classical work of Westheimer.[27] We sought to obtain a semiquantitative estimate of this effect by modifying the system **1** (Y = Me). Data summarized in Table V show that insertion of bromine at C-4 produces an appreciable and apparently constant effect. It must be pointed out that, although bromine is a group of only moderate size, the system **4** (R = Br) is *strongly* buttressed because bromine is further buttressed by the cyclopentene ring. Clearly, the results summarized in Table V could be used in conjunction with the I_{340}^{X-H} values (Table III) and the value of $\Delta S_{av}{}^{*}$ to give semiquantitative estimates of the rotational barriers in a wide range of biphenyl derivatives.

Energy Penalty Associated with Nonbonded Interactions in Biphenyls. So far we have used our results to establish a relationship between the size (or effective size) of molecular fragments and the energy penalty associated with nonbonded interactions involving these fragments. However, the severity of a nonbonded interaction is not determined solely by the size of the interacting molecular fragments, but also by the geometry of the system and its mode of relaxation, in particular its resistivity to bond bending or stretching.

In system **1** the molecular framework is assumed to remain constant as the molecular fragments X and Y change, but the severity of the interactions of the groups X with H-7 and Y with H-6′ depends not only on the effective sizes of X and Y, but also on the lengths of bonds joining these fragments to the skeleton. We wish to propose here a convenient measure of the severity of steric interactions, by introducing the concept of "*apparent overlap*", r^*, which is defined as the projection of the van der Waals radii in a hypothetical (in fact, generally impossible) structure where there is *no* distortion of bond angles and lengths from their typical values. For the series **1** apparent overlap is taken to be negligible in the ground states (criterion 5 above) and the apparent overlap in the transition states is calculated from projections in hypothetical planar states, using standard values for bond lengths and angles[1] and data for effective van der Waals radii obtained in this work (Table II). An example of this geometrical exercise is shown in Figure 5.

For groups with average conical symmetry (CH_3 and CF_3) the bond length C–X was taken to be the calculated distance between the aromatic carbon and the plane defined by the hydrogen or fluorine nuclei. This makes the methyl group a sphere of radius 1.8 Å on a "bond" 1.90 Å long. The nature of this exercise is such that the value of r^* is much less sensitive to the values assumed for bond lengths and angles than to the values of van der Waals radii.

It must be emphasised that r^* is introduced merely as a convenient measure of the severity of nonbonded interactions and gives

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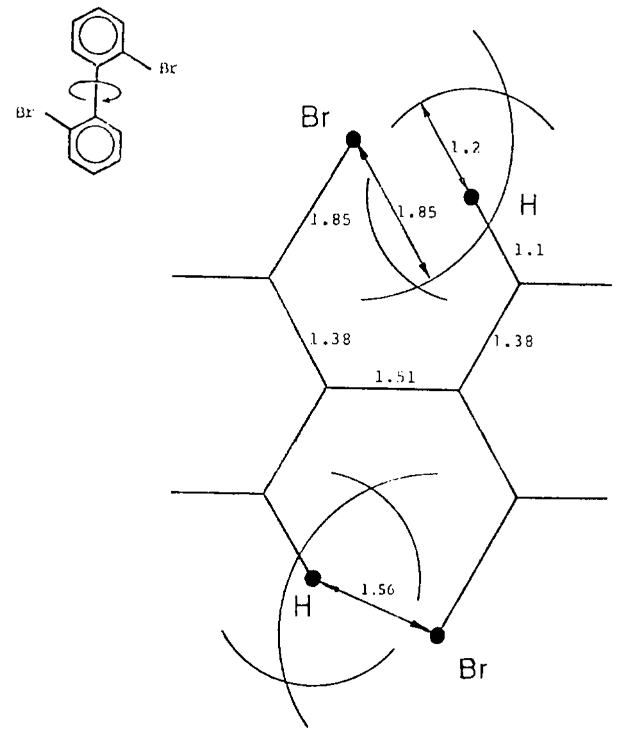


$$\Sigma r^* = 2 \times [(1.85 + 1.2) - 1.56]$$
$$= 2.98\ \text{Å}$$

Figure 5. The contibutions to $\sum r^*$ in 2,2′-dibromobiphenyl. All distances are in Å; all bond anlges are 120°. The equivalence between the van der Waals radius of bromine and the length of the C–Br bond is fortuitous.[1]

no insight whatsoever into the actual details of geometry of the transition state.

The apparent overlaps were assumed to be additive and their values obtained by the above procedure are listed in Table VI together with the appropriate activation energies. It can be seen that the $\sum r^*$ (Å) plotted against $\Delta G_{340}^{\ddagger}$ (Figure 6) gives a good *linear* correlation, in contrast to the plot against van der Waals radii (Figure 3), which is merely monotonic. It must be emphasized that, although we are utilizing (Table VI) the values for effective van der Waals radii previously obtained from rotational barriers, the linear plot (Figure 6) is not due to circular reasoning, because the effective van der Waals radii are very similar (Table II) to those which could be obtained from the published data of Bondi[1] or Charton.[3] This suggests that $\sum r^*$ s a reasonable geometrical parameter for the determination of the severity of steric interactions. We, therefore, decided to explore if the linear relationship defined in Figure 6, which can be expressed by the equation

$$\Delta G_{340}^{\ddagger} = 26 \sum r^* + 4.7 \text{ kJ mol}^{-1} \qquad (1)$$

could also be used to estimate rotational barriers in other systems. Clearly, such systems would have to comply to some extent to the design principles listed in the beginning of this paper; otherwise the geometrical parameters ($\sum r^*$) could not be obtained nor could the experimental energy parameters be usefully compared with the estimated values.

Suitable data which we have been able to locate are summarized in Table VII. The enery barriers for compounds **13a** and **13b** were reestimated in this laboratory and the result for compound **14** refers to the *difference* between the rotational barriers in **14a**

Table VII. Estimation of Rotational Barriers in Systems Other Than Biphenyl Derivatives

ref	compd	Σr^*, Å	energy penalty, kJ mol^{-1}, at 340 K: exptl rotational barrier[a]	estimated from eq 1
this work	5	2.48	62.5 ± 2.1	69
28	6	3.30	102	91
29	6	4.20	115	114
30	6	5.10	128	137
31	7	3.30	106	91
32	8	3.30	98	91
32	9	3.30	97	91
33	10, 11, 12	3.30	93	91
34[b]	13a	2.54	91.4 ± 1	71
34[b]	13b	2.09	84 ± 1	59
35[b]	14	0.25	6.3 ± 3	11

[a] Using reported $\Delta S^{\ddagger}$ values for temperature corrections. [b] See text.

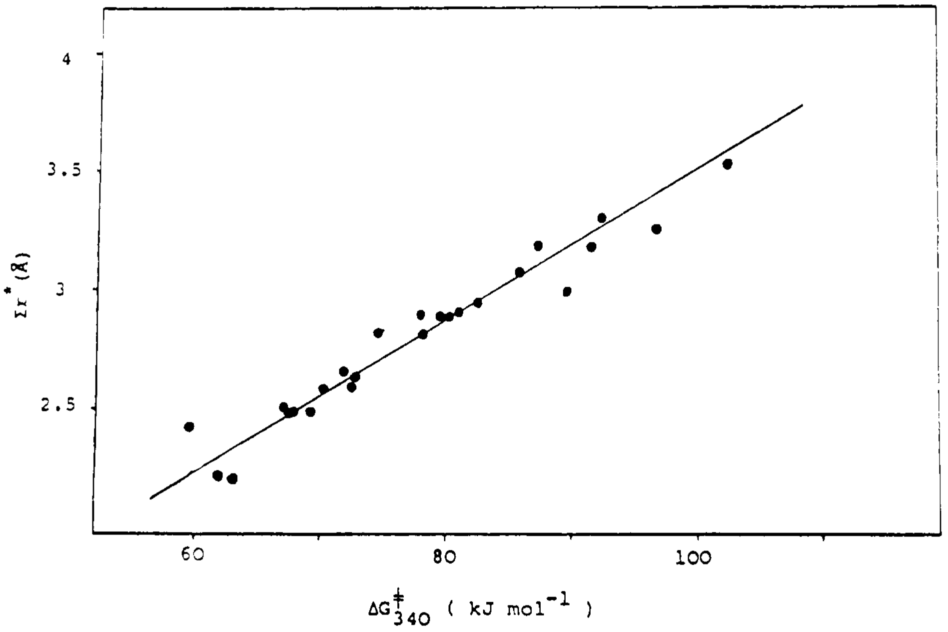
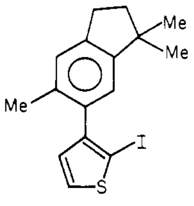


Figure 6. The correlation of $\Delta G^{\ddagger}_{340}$ with the sum of the apparent overlap ($\sum r^*$) for biphenyls. The line indicated is the least-squares line of best fit, slope = 26 kJ mol^{-1} Å^{-1}, correlation coefficient = 0.90. Data are taken from Table VI.

Chart I



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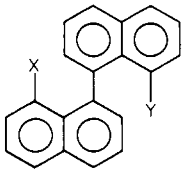
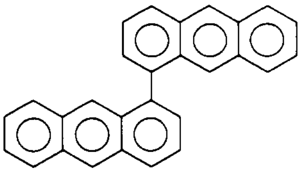


6a, X = Y = H
b, X = H; Y = Me
c, X = Y = Me



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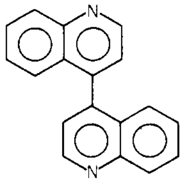

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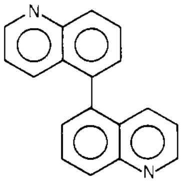

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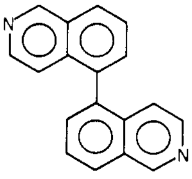

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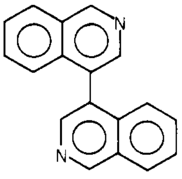

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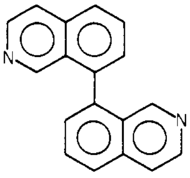

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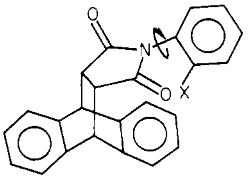
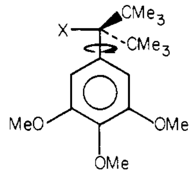


13a, X = Me
b, X = OMe



14a, X = OH
b, X = H

and **14b**.[35] Given the extreme nature of the assumptions made in these estimates (e.g., the neglect of differences in the directions of bonds joining the interacting groups and in the nature of the molecular frameworks) as well as the neglect of the entropy problem, the agreement between the experimental and estimated values (Table VII) is almost fortuitously good. Furthermore, when the results summarized in Tables VI and VII are treated together, a good linear fit can be obtained leading to an equation analogous to eq 1 but with slightly modified parameters.

However, in our view the systematic design of other molecular frameworks is a prerequisite for the investigation of the generality of the relationship of the type embodied in eq 1 and this work is actively pursued in these laboratories.

Experimental Section

Dynamic NMR Spectroscopy. ^1H NMR spectra were obtained at 60 (JEOL FX6OQ), 100 (Varian XL100 FT), and 270 MHz (Bruker HX 270). In all cases temperatures were calibrated by inserting capillaries filled with methanol or ethylene glycol into the sample tubes. Temperatures were obtained from the separation of the hydroxylic and CH resonances by using the equations of Van Geet[36] and Kaplan, Bovey, and Cheng,[37] respectively. All data listed in Table I were obtained from line-shape analysis[17] of the resonances due to the geminal methyl groups in **1**. Particular attention was paid to the following parameters: (i) The slow exchange separation, $\Delta\nu_s$, was found to be solvent dependent (see above) and to have a significant inherent temperature variability[14,35] in nearly all cases. The latter was always carefully taken into consideration in the analysis of data and experimental results are summarized in a separate section below. (ii) The line-shape program[17] was run for the $A_3B_3 \rightleftarrows B_3A_3$ system, rather than for the $A \rightleftarrows B$ approximation, and J_{AB} was accurately determined (0.30 ± 0.005 Hz, an unexceptional value[38]) by preparing appropriately ^2H- and ^{13}C-labeled 1,1-dimethylindan derivatives (see below). (iii) The line widths used as input parameters were the sum of the line width of Me_4Si used as an internal standard, which reflects inhomogeneity of the magnetic field, to which was added an experimentally determined contribution due to T_2 obtained from spectra of a model compound, 1,1,5-trimethyl-6-phenylindan, at the appropriate temperature and in the same solvent.

For some compounds (**16** and **17**, Table I) it was possible to obtain additional kinetic parameters from line-shape analysis of the resonances due to additional prochiral groups and for others (**6**, **20**, and **33**, Table I) coalescence points of the ^{13}C resonances due to the *gem*-dimethyl groups were obtained from 20-MHz spectra (Varian CFT 20, temperatures checked by substitution with Wilmad thermometers).

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Supplementary Material Available: Data concerned with general experimental procedures, synthesis of individual compounds, and experimental data for slow exchange separations of prochiral groups at various temperatures and in various solvents (61 pages). Ordering information is given on any current masthead page.

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