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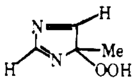

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Interdependence of Solvolysis Rate and Aryl–Aryl Dihedral Angle in a Series of 4-Biphenylyldimethylcarbinyl *p*-Nitrobenzoates

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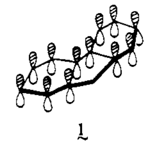
Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. *Received May 7, 1979*

Abstract: 4-Biphenylyldimethylcarbinyl *p*-nitrobenzoate and four 2,2′-bridged analogues (1–4 methylene groups) were synthesized and their rates of solvolysis in 80% aqueous acetone determined in order to establish whether there exists in these systems a correlation between kinetic behavior and aryl–aryl dihedral angle. The relative rates at 60.4 °C are as follows: $n = 0$, 1; $n = 1$, 17.6; $n = 2$, 4.3; $n = 3$, 1.8; $n = 4$, 1.1. To gain added insight, the ^{13}C NMR spectra of the *tert*-cumyl cations were also recorded in FSO_3H–SO_2ClF at −90 °C. The (^+C) ^{13}C NMR shifts correlate in linear fashion with $\cos^2\theta$ ($r = 0.985$), the good data fit clearly indicating a systematic attenuation of charge distribution and implicating the dihedral angle as an important factor in delocalization. In contrast, the rate constant for the fluorenyl analogue fails to correlate with the ^{13}C chemical shift of its cation; it appears to be more reactive than expected on this basis. The results argue for consideration of a decrease in θ for all systems *except fluorenyl* during conversion to the corresponding cation, in an effort to better accommodate the positive charge. Importantly, the linear plot requires that a *proportionate* decrease in θ of similar magnitude be ultimately adopted by **7, 9, 10,** and **11.** The enhanced solvolytic rate of the fluorenyl example can then be traced to entropic factors.

The physical basis and limits of homoconjugative interaction, particularly in charged systems, have been a source of fascination to chemists for 20 years.[2] Although precise three-dimensional structural information is still lacking, the extent of interpenetration of the relevant orbitals in such systems (and consequently the resultant overlap integral) is thought to be dependent on internuclear distance and relative spatial orientation.[3]



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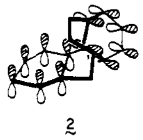

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As an extension of our own involvement with extended homoaromaticity,[3,4] we have presently assessed the relative reactivities of a series of biphenyls bridged at positions 2 and 2′ with hydrocarbon chains composed of one to four methylene units. As denoted in the three-dimensional representations of the limiting extremes indane (**1**) and dibenzo[*a,c*]cyclooctadiene (**2**), the principal effect of enlarging the methylene bridge in incremental steps is to twist about the central biphenyl σ bond so as to generate progressively larger angles without greatly perturbing the internuclear distance. Since electronic interaction between the two phenyl rings is presumably dictated in large part by overlap of the π orbitals positioned at C-1 and C-1′, the geometrically imposed twist on this central axis should directly affect the level of interring conjugation. In the

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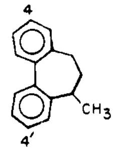
present investigation, we have sought quantitative data which would reveal the magnitude of residual resonance capability within a given biphenyl which is forced to adopt a relatively rigid conformation.

There exist two convenient methods by which the relative reactivities of polynuclear aromatic molecules can be determined. The first comprises kinetic investigation of a suitable electrophilic substitution reaction, the second a study of an appropriate side-chain reaction. The former approach has been pioneered by Brown,[5] de la Mare,[6] and Eaborn[7] whose groups have carried out a comprehensive series of measurements concerned chiefly with the relative rate behavior of biphenyl and fluorenyl systems. Established by these investigations was that planar fluorene is approximately 200 times more reactive than the noncoplanar biphenyl.[8] Additionally, de la Mare, Johnson, and Lomas have pointed out that the orientation of chlorinative substitution in **3** and **4** continues to occur at the 4 and 4′ positions, electron release from the second aryl ring therefore remaining large enough to retain domination over the alkyl side chain.[6a] The London group concluded that "the change toward planarity in the transition state, if it is substantial for any of these compounds, is likely to be substantial for all of them". At the time, the available data did not permit a rigorous test of this proposal.



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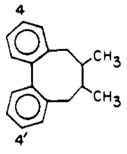

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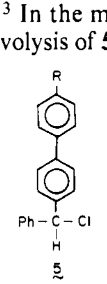
In a similar vein, Eaborn and his co-workers adduced from examination of protodesilylation rates that the noncoplanarity of the rings in biphenyl does not affect the transmission of electronic effects. On the basis of these results, they suggested that "the effects of substituents on the transition state are likely to be much more important than those on the initial state, and the two rings [in biphenyl] are probably near coplanarity in the transition state".[7]

On the other hand, Stock and Brown interpreted their findings in terms of a variable and depressed resonance stabilization of the activated complex in biphenyls, the inhibition of resonance being due to the steric barrier for achieving coplanarity of the phenyl rings.[9]

The solvolytic approach has been shown to be an important tool for interrelating the effects of polyaromatic structure and chemical reactivity chiefly by Berliner,[10] Bolton,[11] Brown,[12] and Tsuno.[13] In the most recent work by Bolton and Burley involving solvolysis of **5** and **6** in ethanol-acetone (9:1),[11c] the slopes of plots of log k (first-order rate constants, 25 °C) vs. σ^+ revealed ρ^+ for **5** (−1.20) to be somewhat more positive than that for **6** (−1.7). The fluorene system does therefore transmit greater electronic effect across the two phenyl rings than does biphenyl, in agreement with the concept that delocalization of charge and interplanar angle are linked.



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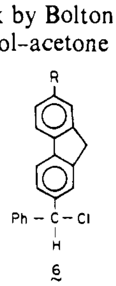

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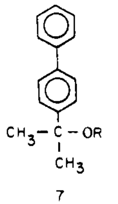
Brown and Inukai interpreted the quantitative aspects of the solvolysis of several *tert*-cumyl chloride derivatives to be an indication that the incipient carbonium ions in the various transition states must be able to accommodate deviations from coplanarity with only minor costs in energy.[12b] The Tsuno group has concluded on the basis of their LArSR relationship (the Yukawa-Tsuno equation[14]) that there exists a more efficient transmission of π-electronic effects in the fluorenyl than the biphenyl system.[13]

Because of the significance of attaining an understanding of the extent to which phenyl rings can relate electronically when held at diverse dihedral angles, we have systematically examined the solvolytic behavior of the five dimethylcarbinyl *p*-nitrobenzoates **7b–11b**. The breadth of the series is self-evident. The *tert*-cumyl *p*-nitrobenzoate derivatives were selected as a consequence of their well established response to ionization in general[15] and because greater demand for charge delocalization was expected to be placed on the biphenyl moiety relative to the benzhydryl chloride derivatives examined by Moore and Starks.[16]



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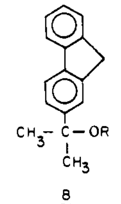

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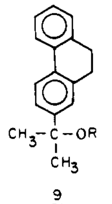

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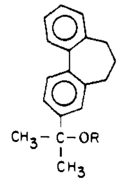

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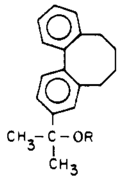

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a, R = H; **b**, R = PNB; **c**, R = CH_3

Like its predecessors, the present solvolytic study suffers from the weakness that information is obtained primarily on the energy difference between initial and transition states, notwithstanding the Hammond postulate which justifies direct comparison of S_N1 transition states and actual carbonium ion intermediates.[17] For this reason, alcohols **7a–11a** have also been converted to their respective carbocations under stable long-life conditions and observed spectroscopically. The resultant relationship between ^{13}C chemical shift and electronic density at the cationic center has been found to provide a very useful point of reference for interpreting the solvolytic data.

Results

Synthesis. The tertiary alcohols were prepared by Friedel-Crafts acetylation of the parent hydrocarbons and subsequent addition of methylmagnesium iodide. The *p*-nitrobenzoates were obtained by reaction of the alcohols with *p*-nitrobenzoyl chloride in dry pyridine. The properties of these derivatives are compiled in Table I.

Kinetics. The rates of solvolysis of **7b–11b** were determined in 80% aqueous acetone by using a standard titrimetric procedure. The kinetic data, together with activation parameters, are collected in Table II.

Product Studies. After solvolysis of **7b–11b** in 80% aqueous acetone to approximately 20 half-lives, each product was isolated and characterized as the respective unrearranged alcohol by spectroscopic methods. Methanolysis of **7b–11b** gave only the corresponding methyl ethers (Table III). The absence of alcohols in the latter series of experiments is indicative of exclusive alkyl-oxygen cleavage. Therefore in the more ionizing aqueous acetone solvent system ($Y = -0.673$ as compared with −1.097 for pure methanol),[18] these esters can be assumed to be ionizing completely to the tertiary carbocations.

Carbonium Ion Generation under Long-Life Conditions. The *tert*-cumyl alcohols dissolved in CD_2Cl_2 were mixed with an

Table I. Physical and Spectral Properties of the *p*-Nitrobenzoates

compd	mp, °C	anal. calcd	anal. found	ν_{max}^{KBr}, cm^{-1}	^{1}H NMR (60 MHz, CDCl$_3$, δ) aromatic	methylene	methyl
7b	134–135	C, 73.12 H, 5.30	C, 73.25 H, 5.56	1740, 1540, 1345, 1260, 1095, 835, 760, 710	8.10 (s, 4 H) 7.6–7.2 (m, 9 H)		1.97 (s, 6 H)
8b	124–125	C, 73.99 H, 5.13	C, 74.02 H, 5.22	1710, 1525, 1340, 1295, 1140, 730, 715	8.13 (s, 4 H) 7.8–7.1 (m, 7 H)	3.83 (s, 2 H)	2.03 (s, 6 H)
9b	107.5–108.5	C, 74.41 H, 5.46	C, 74.46 H, 5.42	1715, 1530, 1350, 1295, 1120, 835. 735, 715	8.12 (s, 4 H) 7.8–7.1 (m, 7 H)	2.85 (s, 4 H)	1.98 (s, 6 H)
10b	103–104	C, 74.80 H, 5.77	C, 74.88 H, 5.92	1725, 1530, 1345, 1285, 1095, 840, 760, 715	8.13 (s, 4 H) 7.4–7.1 (m, 7 H)	2.65–2.2 (m, 6 H)	2.00 (s, 6 H)
11b	125–126	C, 75.16 H, 6.07	C, 75.22 H, 6.16	1725, 1530, 1350, 1285, 1090, 840, 750, 715	8.12 (s, 4 H) 7.18 (br s, 7 H)	3.0–2.0 (m, 8 H)	2.00 (s, 6 H)

Table II. Kinetic Data for the Solvolysis of **7b–11b** in 80% Acetone

compd	*T*, °C	$k_1 \times 10^5$, s^{-1}	F_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol (60.4 °C)	$\Delta S^{\ddagger}$, eu (60.4 °C)	k_{rel} (60.4 °C)	k_1 (25 °C), s^{-1} [a]
7b	79.0	34.95	25.9	25.2	−3.1	1	4.3×10^{-7}
		34.80					
	70.0	13.71					
		13.05					
	60.4	4.62					
		4.27					
8b	60.4	82.68	25.1	24.4	1.9	17.6	8.8×10^{-6}
		74.32					
	50.2	24.05					
		24.01					
	39.7	6.53					
		6.31					
9b	70.0	59.99	24.8	24.1	−3.4	4.3	2.3×10^{-6}
		54.49					
	60.4	19.50					
		19.21					
	50.2	6.30					
		6.06					
10b	80.0	63.22	24.2	23.6	−6.7	1.8	1.1×10^{-6}
		60.60					
	70.0	26.08					
		25.11					
	60.4	8.26					
		8.03					
11b	80.0	44.64	26.2	25.5	−2.1	1.1	4.3×10^{-7}
		40.00					
	70.0	13.95					
		13.32					
	60.4	4.73					
		4.70					

[a] Extrapolation made on the basis of the activation parameters.

equal volume of FSO$_3$H-SO$_2$ClF (1:1 v/v) at −140 °C in 10-mm tubes. The ^{13}C NMR spectra of the resultant red solutions were recorded at −90 °C. The chemical shifts of the cationic and methyl carbons are compiled in Table IV alongside values for the magnitude of the dihedral angle between the phenyl rings.

In view of the inherent conformational flexibility of biphenyl systems, one must take account of possible environmental effects on conformation. Biphenyl itself has been most widely studied in this regard. X-ray diffraction has indicated that the hydrocarbon is planar in the solid phase,[19] a conclusion also arrived at on the basis of Kerr constant studies in solution.[20] The latter interpretation does not at all conform to early ultraviolet measurements from which variable θ values of 20–30° depending upon solvent were deduced.[8] More recent investigations using electron diffraction[21] and photoelectron spectroscopic techniques[22] have determined the angle to be 45°, in good agreement with the best fit realized in molecular chlorination studies.[6a] For these reasons, biphenyl is generally viewed as having a broad and rather shallow potential-energy

Table III. Spectral Properties of the Methyl Ethers **7c–11c**

compd	*m/e* calcd	*m/e* obsd	$\nu_{\max}^{\text{neat}}$, cm^{-1}	^{1}H NMR (60 MHz, CDCl$_3$, δ) aromatic	methylene	methoxyl	methyl
7c ($C_{16}H_{18}O$)	226.1358	226.1354	1255, 1165, 1070, 830, 760	7.5–7.1 (m, 9 H)		3.00 (s, 3 H)	1.50 (s, 6 H)
8c ($C_{17}H_{18}O$)	238.1358	238.1364	1265, 1170, 1075, 770, 735	7.8–7.2 (m, 7 H)	3.83 (s, 2 H)	3.10 (s, 3 H)	1.62 (s, 6 H)
9c ($C_{18}H_{20}O$)	252.1514	252.1521	1250, 1170, 1070, 770, 730	7.8–7.1 (m, 7 H)	2.88 (pseudo s, 4 H)	3.13 (s, 3 H)	1.58 (s, 6 H)
10c ($C_{19}H_{22}O$)	266.1671	266.1676	1255, 1170, 830, 7.55	7.5–7.1 (m, 7 H)	2.88–2.2 (m, 6 H)	3.27 (s, 3 H)	1.60 (s, 6 H)
11c ($C_{20}H_{24}O$)	280.1827	280.1835	1255, 1170, 825, 745	7.17 (narrow m, 7 H)	3.0–1.8 (br m, 8 H)	3.28 (s, 3 H)	1.60 (s, 6 H)

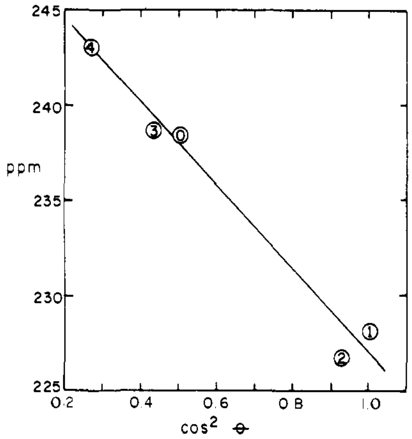


Figure 1. Plot of ($^+$C) ^{13}C NMR chemical shift (ppm downfield from Me_4Si) vs. cos^2 of angle between the two phenyl rings in **7**$^+$–**11**$^+$. The numerals inside the circles refer to the number of methylene groups in the 2,2′ bridge.

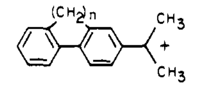
curve restricting rotation about the coplanar position.[23] Adoption of the Westheimer–Mayer model for the racemization of optically active biphenyls has led to a calculated value of 3.9 kcal/mol for the barrier to free rotation.[24] Table IV shows that an assumed angle of 45° conforms nicely to the linear correlation of ($^+$C) ^{13}C NMR shift and cos^2 θ.

An X-ray analysis of fluorene by Burns and Iball[25] has shown the molecule to have a strained planar geometry (θ = 0°). Of particular interest is their finding that the interconnective aryl–aryl bond (1.48 Å) is somewhat shorter than the same bond in biphenyl (1.52 Å). This has been considered by some to be a direct reflection of the greater double bond character and enhanced conjugative interaction between the phenyl rings when the monomethylene bridge is present.

Over the years, the twist angle of 9,10-dihydrophenanthrene has been variously estimated. An early theoretical calculation by Jones[26] which generated a value of 15° was later reinforced by de la Mare[6] who concluded 16° to be appropriate. This value is in reasonable agreement with claims of 18° derived by Braude and Forbes from ultraviolet studies,[27] of 21° by Maier and Turner based upon photoelectron spectroscopic measurements,[22] and of 24° by Unanue and Bothorel as a consequence of Rayleigh scattering experiments.[28] Herein, we shall see that a dihedral angle of 16° conforms best to our ^{13}C NMR shift data.

A θ value of 49° has been calculated by Beaven for dibenzo-1,3-cycloheptadiene from standard bond lengths and angles,[29] successfully utilized by de la Mare in halogenation studies of **3**,[6] and estimated presently from Dreiding models. Calculations on dibenzo-1,3-cyclooctadiene have generated a molecular geometry having θ = 59°. In view of the support these values have received,[6,16] they have been utilized in this investigation.

Table IV. ^{13}C NMR Chemical Shifts (ppm, CD_2Cl_2, FSO_3H, SO_2ClF, −90 °C) of $^+$C and Methyl Carbons in the *tert*-Cumyl Cations, and Dihedral Angle (θ) between the Planes of the Aromatic Rings



n	$^+$C, ppm	CH$_3$, ppm	θ, deg
	238.61	31.37	45
1	228.21	30.27	0
2	226.78	29.10	16
3	238.80	30.85	49
4	243.09	31.70	59

Discussion

Relationship of Bridge Length and Dihedral Angle to ^{13}C Shifts. Examination of the ($^+$C) ^{13}C chemical shifts of the five 4-biphenyldimethylcarbinyl cations **7**$^+$–**11**$^+$ reveals the existence of an excellent linear relationship with cos^2 θ. The correlation coefficient of the plot shown in Figure 1 is 0.985. The good data fit clearly indicates a systematic trend of charge distribution[30,31] and implicates the prevailing dihedral angle as an important factor in positive charge delocalization within these ions. Although difficulties have been encountered by others in placing on a quantitative basis those factors that influence the ^{13}C shift in *different types* of carbocations,[15a,32,33] it has not been our intention to prove the widely accepted structural features of the *tert*-cumyl cationic center, but only to relate its ^{13}C NMR shift to charge density. Because a closely related family of tertiary carbocations is involved, we believe the present estimates of *relative* charge distribution to be empirically sound. The existence of a linear relationship of *tert*-cumyl cation ^{13}C chemical shifts with σ^+ constants[34] is strongly supportive of our position.

It is generally considered[35] that the extra stabilization energy E potentially available to two linked aryl systems is related to the angle θ between their planes by the equation

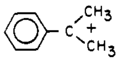
$$E = E_0 \cos^2 \theta$$

Strictly speaking, the equation can be correctly applied in the present context only to **8–11**, for **7** lacks a *m*-alkyl substituent. Additionally, it must be assumed that the effects of the 2,2′-alkyl groups on charge density (as well as ionization rate) will prove constant regardless of the value of *n*. Since the σ^+ constants for *m*-methyl (−0.0652) and *m*-ethyl (−0.0625) are closely comparable,[36] this assumption is easily accommodated.

The extra resonance energy for planar biphenyl[37] and for fluorene[38] has been independently estimated to be 5 kcal/mol. Using this value as an indicator of the order of magnitude, we compute from Table IV and Figure 1 that the inter-aryl ring conjugation is progressively reduced to 4.6, 2.2, and 1.3

kcal/mol as the number of methylene groups is increased from two to three and then four.

It was observed that the ($^{+}$C) ^{13}C chemical shift of 7^{+} compares very closely with that of $\mathbf{10}^{+}$. Since this is as expected on the basis of their entirely similar δ values, it would appear that the electronic impact of the 2,2′-methylene chain is inconsequential relative to the dihedral angle, at least at this level of sophistication.



12

Olah and White have previously established the ($^{+}$C) ^{13}C chemical shift of the phenyldimethylcarbonium ion (**12**) to be 254.4 ppm.[32a] Since the values for 7^{+}–11^{+} all appear at higher field, it is clear that the biphenyl moieties in the latter group of cations are considerably more electron releasing than hydrogen, irrespective of the interplanar angle. A very interesting point of reference would be provided if a biphenyl derivative having two rings held perfectly perpendicular ($\theta = 90°$, $\cos^2 \theta = 0$) could be synthesized. This is not feasible by mere extension of the present approach because additional increases in the degrees of freedom of the bridge are expected to decrease rather than increase the energy required to achieve coplanarity.

Effect of Bridge Length on Solvolysis Rate. 4-Fluorenyldimethylcarbinyl *p*-nitrobenzoate (**8b**) reacts 17.6 times faster than the 4-biphenylyl derivative **7b** at 60.4 °C, the common temperature selected for all systems investigated (Table II). Thus, the energy barrier to ionization is again seen to be lowered in the case of the planar molecule, although the reactivity range is rather small. Since the kinetic behavior of the 1,3-dibenzocyclooctadienyl *p*-nitrobenzoate **11b** compares closely with that of **7b**, one could conclude that the four methylene groups in **11b** are effective in maintaining a dihedral angle between the phenyl rings closely comparable to that which prevails in the biphenyl analogue at the respective transition states. In view of the intermediate responses of **9b** and **10b**, the solvolytic reactivity order would appear internally consistent in revealing that electron supply to the developing electron deficient center decreases as *n* increases from 1 to 4. The differences in the entropies of activation for **7b**, **9b**, **10b**, and **11b** are likely due to experimental uncertainties, and probably should be regarded as very nearly constant (−5 ± 1.5 eu). In view of the generally negative character of these $\Delta S^{\ddagger}$ values, it is reasonable to consider the transition states for these four systems as more restricted in their degrees of motion than the ground states. The major source of constraint would appear to be rotation about the aryl σ bond so as to compress θ, a conclusion supported by the positive entropy term associated with fluorenyl system **8b** wherein rotation is not possible.

In order to determine if some of the entropy decrease also arises from twisting of the molecules toward coplanarity in the solvolysis transition states, a plot of log $k_{\rm rel}$ (60.4 °C) vs. ($^{+}$C) ^{13}C chemical shift was constructed (Figure 2). This very revealing diagram shows that the straight line which interconnects the higher bridged systems (n = 2-4) fails by a substantial margin to encompass the reactivity of the fluorenyl derivative. Unbridged biphenyl analogue **7b** which is denied the benefit of alkyl substitution deviates only to a small extent from the line. This is considered to be a reflection of proportionately comparable interring twisting at the transition state when n = 0 and 2-4, but not 1.

Thus, the fluorenyl system appears to be exceptionally effective in stabilizing the *incipient* carbonium ion. The correlation of Figure 2 implies that similar requirements are made of the hydrocarbon moiety in each reaction, but that **8b** responds more readily under solvolytic conditions. This is attributed to the absence of a change in θ in the latter example, which is essentially locked at 0° with resultant "exceptionally good" resonance interaction (see Figure 1). The higher homologous bridged systems and the biphenyl derivative give indication of striving toward improved aryl-aryl pπ overlap, but never attain $\theta = 0°$ for steric reasons. As Figure 1 reveals, the positive charge is accommodated by a proportionate decrease in θ of a *similar order of magnitude* in **7**, **9**, **10**, and **11**. This phenomenon also operates during solvolysis if the entropies of activation for these four systems adequately probe the ground state–transition state structural perturbations as they must. Thus, the kinetic acceleration observed upon bridging the biphenyl ring system with a single methylene group is unique in that little, if any, structural movement between the aryl rings materializes; therefore, no rate-retarding negative entropy features gain importance in this case.

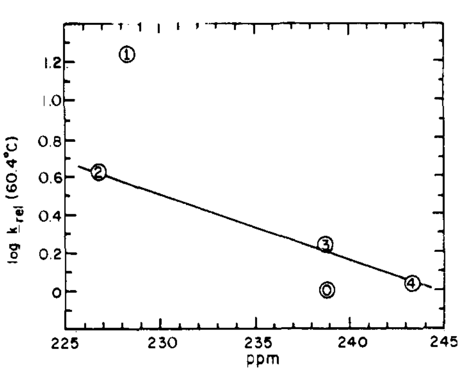
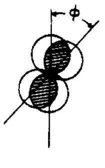


Figure 2. Plot of log $k_{\rm rel}$ (60.4 °C) vs. ($^{+}$C) ^{13}C NMR chemical shift (ppm downfield from Me_4Si). The numerals inside the circles refer to the number of methylene groups in the 2,2′ bridge.

Summary

The pair of phenyl rings in **7** and 2,2′-bridged biphenyl systems **9–11** have the capability of approaching coplanarity when existing as *tert*-cumyl carbocation solutes in superacid solution or during solvolysis. Evidence has now been found that such increased resonance interaction gains substantive importance. The level of extended charge delocalization in such molecules can be attenuated seemingly at will by simply adjusting the size of the methylene bridge to give the proper θ value. The observed variation in θ upon ionization is narrowly defined, directly proportionate to ground state θ, and not at all random. The only anomaly is fluorene whose derivatives are exceptionally reactive in solvolysis due to structural inflexibility.

As seen from the ($^{+}$C) ^{13}C NMR shift data for 7^{+}–11^{+} in relation to that of **12**, rather substantial deviations from coplanarity do not destroy all of the interring resonance energy. This signifies that considerable overlap of the C-1 and C-1′ p orbitals is maintained even though they are twisted to a measurable degree out of coplanar alignment.[39]



As a consequence of these findings, it is clear that the effect of charge density on ^{13}C shifts can be put on a relative quantitative basis in a closely related series of compounds and that such an approach can be used to advantage as a diagnostic probe of transition state structural features in cation-forming reactions.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer and the ^{1}H NMR spectra were determined with a Varian T-60 instrument. Mass spectra were measured on an AEI-MS9 spectrometer at an ionization of 70 eV. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

4-Biphenylyldimethylcarbinol (7a) was prepared by a modification (see text) of the procedure of Moury and co-workers.[40]

2-Fluorenyldimethylcarbinol (8a). To a ice-cooled stirred slurry of magnesium turnings (3.34 g, 138 mg-atoms) in 40 mL of anhydrous ether was added dropwise a solution of methyl iodide (19.54 g, 138 mmol) in the same solvent (40 mL). Upon completion of the addition, the reaction mixture was stirred at room temperature for 12 h before being treated with a solution of 2-acetylfluorene[41] (14.32 g, 68.8 mmol) in dry tetrahydrofuran at 0-5 °C. The contents were stirred for 1.5 h at 0-5 °C, 2 h at 25 °C, and 6 h at 40-50 °C. After cooling, this mixture was poured onto ice and saturated ammonium chloride solution. The product was extracted into ether (3 × 50 mL) and the combined organic layers were washed with saturated ammonium chloride solution and water prior to drying. The solvent was evaporated to give 13.3 g of unpurified **8a** (mp 110-113 °C) which was directly converted to the *p*-nitrobenzoate.

Preparation of *p*-Nitrobenzoates. General Procedure. A solution of **8a** (8.34 g, 45 mmol) in dry pyridine (50 mL) cooled to 5 °C was treated with 8.34 g (45 mmol) of *p*-nitrobenzoyl chloride. After 3 h, the reaction mixture was allowed to warm to room temperature for 16 h. The product was extracted into dichloromethane, washed with water, 1 M hydrochloric acid, 5% aqueous sodium bicarbonate solution, and water before drying. Evaporation left a pale yellow solid which was recrystallized from carbon tetrachloride to give pure **8b**. For properties, see Table I.

2-Acetyl-9,10-dihydrophenanthrene was prepared according to the directions given by Burger and Mosettig.[42]

4-Acetyl-2,2′-trimethylenebiphenyl. To a solution of dibenzo-1,3-cycloheptadiene[16,43] (12.0 g, 0.063 mol) in dry carbon disulfide (50 mL) was added anhydrous aluminum chloride (16.7 g, 0.125 mol) in one portion. Four drops of acetic anhydride was introduced to the vigorously stirred reaction mixture and the flask was warmed on a steam bath to initiate reaction. The remainder of the acetic anhydride (6.4 g, 0.063 mol) was added at such a rate that the carbon disulfide refluxed gently. Upon completion of the addition, the mixture was heated on the steam bath for 1 h, cooled, and slowly added to a beaker containing water (100 mL) and concentrated hydrochloric acid (4 mL). The product was taken up in dichloromethane and the combined organic layers were washed with water and saturated sodium bicarbonate solution before drying. Solvent removal left 13.55 g (92%) of a yellowish viscous liquid which crystallized on standing. Recrystallization from hexane gave colorless crystals, mp 67-68 °C.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.33; H, 6.78. Found: C, 86.12; H, 6.57.

4-Acetyl-2,2′-tetramethylenebiphenyl. Analogous treatment of dibenzo-1,3-cyclooctadiene[16,44] (7.9 g, 0.038 mol) afforded the 4-acetyl derivative in 59% yield as a colorless crystalline solid, mp 120-121 °C (from 95% ethanol).

Anal. Calcd for $C_{18}H_{18}O$: C, 86.40; H, 7.20. Found: C, 86.23; H, 7.18.

Kinetic Studies. Preparation of Reagents. Acetone was prepared by distillation from potassium permanganate and redistillation after drying over anhydrous potassium carbonate. Doubly distilled water was employed. Methanol was prepared by distillation from magnesium methoxide.

General Kinetic Procedure. The methodology employed followed that described earlier.[45]

Preparative Scale Solvolysis. General Method. A solution of **8b** (107.8 mg, 0.29 mmol) and 2,6-lutidine (0.2 mL) in 80% aqueous acetone (50 mL) was heated at 40 °C for approximately 20 half-lives. The reaction mixture was concentrated under reduced pressure and the resulting suspension was extracted with dichloromethane. The organic phase was washed with sodium bicarbonate solution and water prior to drying. Solvent removal gave 64 mg (98%) of a pale yellow solid whose spectra were superimposable upon these of **8a**.

Methanolysis Studies. In a typical procedure, 114.4 mg (0.306 mmol) of **8b** was dissolved in anhydrous methanol (50 mL) containing 0.2 mL of 2,6-lutidine and the mixture was heated at 60 °C for 70 h. After removal of the methanol under reduced pressure, the resulting semisolid was leached with dichloromethane. The organic layer was processed in the predescribed manner to give 68.9 mg (94%) of **8c** (see Table III).

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Variable Transition State Structure in 3,3-Sigmatropic Shifts from α-Secondary Deuterium Isotope Effects

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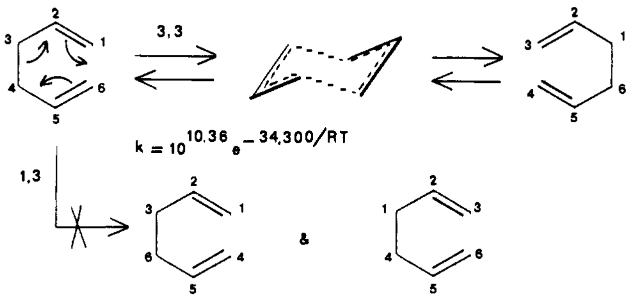
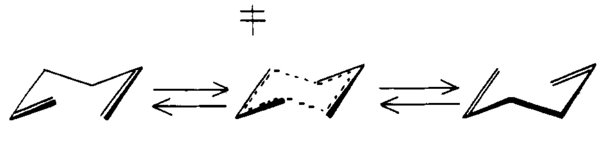
Abstract: The relative values of secondary α deuterium kinetic isotopic effects at the terminal and central carbons of 1,5-dienes undergoing the 3,3-shifts vary as a function of substitution. With radical stabilizing groups on C_3, the transition state more resembles two weakly coupled allyl radicals. With radical stabilizing substituents at C_2 and C_5, the transition state more resembles cyclohexane-1,4-diyl. A thermochemical argument renders unlikely cyclohexane-1,4-diyl as an intermediate in the 3,3 shift of 1,5-hexadiene. Comparison of the KIEs at C_4 and C_6 in the rearrangement of 3-oxa-1,5-hexadiene (allyl vinyl ether to 4-pentenal) to appropriate equilibrium isotope effects reveals that the transition state "comes early" with more bond breaking than making. The transition state structures for many 3,3 shifts are discussed in terms of the relative stabilities of the two nonconcerted alternatives arising from either complete bond breaking or complete bond making.

Introduction

The double allylic rearrangement of 1,5-hexadienes discovered by Hurd[1a] and by Cope[1b] is a facile thermal reaction which is accompanied by a single allylic rearrangement only when the terminal carbons cannot strongly interact.[2]



Early speculation on the mechanism of the rearrangement of 1,5-hexadiene focused on a concerted process whose transition state involved C_1–C_6 bond formation assisting C_3–C_4 bond cleavage.[1e] Doering and Roth provided evidence for a four center, "chair", transition state,[3] and, though a "twist" or "helix" arrangement could also rationalize the data,[4] an asymmetry transfer experiment by Hill rejects all but the chair arrangement of atoms in the lowest energy pathway for the reaction.[5] Doering subsequently determined the activation parameters for the reaction in 1,5-hexadiene itself ($\log k = 10.36 - 34\,300/2.3RT$) and raised the specter of a nonconcerted two-step pathway via cyclohexane-1,4-diyl whose estimated heat of formation is near that for the transition state of the Cope rearrangement.[6] The stereochemical observations could then be rationalized in terms of favored formation and decomposition of a chair-like diyl. The chair diyl also appears to be involved in the thermolysis of



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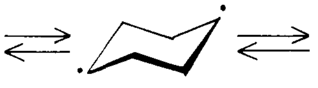
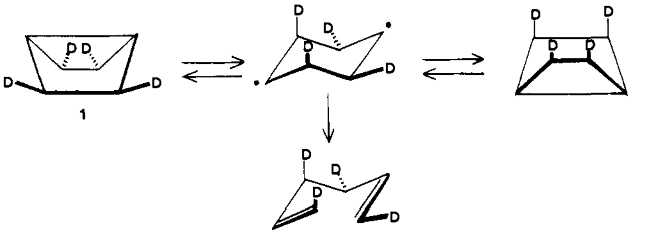


intermediate

bicyclo[2.2.0]hexane, **1**, which undergoes cleavage to 1,5-hexadiene with high stereospecificity and bridgehead double inversion,[7] although Goldstein indicates that both bridgehead double inversion and cleavage could be separate concerted processes.



meso cis trans

In support of the diyl hypothesis of the 3,3 shift is Dewar's observation that 2-phenyl and 2,5-diphenyl-1,5-hexadiene rearrange 69 and 4900 times faster, respectively, than the parent indicating some radical character at C_2 and C_5 in the transition state.[8] Wehrli and Schmidt made similar observations with 2,5-dicyano-1,5-hexadiene, and since activation free energies for the dicyano materials were (somewhat) lower than for the diphenyl materials, the suggestion was made that the diyl is more favorable in the dicyano case.[9] Wehrli and Schmidt also recognized that the Cope rearrangement transition state structure could be dependent on substitution, a point that is the major focus of this paper.

In addition to the experimental work with the phenylhexadienes, Dewar found that the MINDO/3 calculated energy surface for the rearrangement of the parent diene puts the diyl (with significant distortions of the C_2- and C_5-bond angles) in a potential energy well 5–15 kcal/mol deep relative to an unsymmetrical transition state linking it to 1,5-hexadiene.[10] Moreover, the transition state is "displaced to a remarkable

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