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The Structural Factors and Reactivity of Biphenyl

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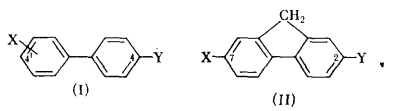
Data on the structure, conformations, and reactivity of biphenyl in solutions have been examined critically and the importance of the conformational factor for the reactivity of biphenyl is repudiated.
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I. INTRODUCTION

The electrophilic substitution and displacement reactions involving a substituent in the 4-position in biphenyl have been widely investigated. A careful study by Stock and Brown [1] has shown that in reactions of this kind biphenyl does not obey the Selectivity Relations for the SE reactions of a series of monosubstituted benzenes. The behaviour of biphenylylene systems (I) in transmitting the electronic influences of substituents to the reaction centre in the 4-position is also unusual. Their capacity for transmitting such effects is greatly reduced compared with the corresponding phenylene and certain bridged structures, where the aromatic rings are separated by an atom with a lone electron pair [2,3]:



(I) (II)

The cause of most of these specific phenomena has been recognised [1,2] as the non-coplanarity of the aromatic rings of biphenyl in solution, which may appreciably disrupt the conjugation between them. The possibility of the system becoming coplanar in the transition state has been regarded as significant [1,2]. In particular, a confirmation of this hypothesis has been seen in the greater reactivity of the 2-position of the planar fluorene molecule (II, X = Y = H) when account is taken of the possible influence of the methylene units and also, seemingly, in the fact that fluorene obeys satisfactorily the Selectivity Relations for a series of monosubstituted benzenes [1]. On the other hand, the possibility of different degrees of conjugation between the non-attacked ring and the reaction centre as a function of a measure of the electrophilic properties of the reactant has been postulated for biphenyl [4-6]. The conformational factor was not regarded as of decisive importance [5,6], but the evidence for this was probably insufficient [1,6].

II. CONFORMATIONAL ANALYSIS OF BIPHENYL

Numerous studies have been devoted to the problem of the steric structure of biphenyl. In the crystalline state the benzene rings are located in the same plane [7-15]. The rings in the biphenyl molecule in the vapour state are not in the same plane and the dihedral angle between their planes is 42–45° [16-19]. The non-planar conformation of the isolated molecule has been explained theoretically as a consequence of the repulsion of atoms not linked by valence forces [20-31].

Direct X-ray and electron diffraction methods, which are effective in the determination of the conformations in the crystalline and vapour states of biphenyl, are unsuitable for its solutions. The results obtained by other methods are contradictory, but the reasons for this have not been discussed. The appreciably lower degree of displacement from coplanarity or even the absence of coplanarity for the molecule in solution compared with the vapour state can be readily accounted for. The low energy barrier to the rotation of the biphenyl rings from the equilibrium to the planar disposition, which amounts to 0.4–4.0 kcal mole^{-1} according to various estimates [21-23,26,27,29,31-34], is evidently overcome when the molecules are packed to form crystals. Since the effective volume of the molecule with the coplanar disposition of the rings is smaller than for the non-coplanar disposition, the internal pressure factor of the solvent should promote the former [35]. The dependence of the conformation of biphenyl, determined from vibrational spectra, on the nature of the solvent has been stressed [36]. The planar conformation of the solute molecule predominates in a structured solvent forming hydrogen bonds, probably owing to the ordering of the species in the environment or owing to unexplained specific effects. Thus the nature of the medium may be responsible for the ambiguity of the results of conformational analysis.

In the number of studies dealing with the vibrational spectra of biphenyl in solutions and in the melt, a qualitative conclusion was reached that the molecules are to some extent non-coplanar [37-42]. The angle of twist of the molecule has been estimated as 22–45° from the shift or changes in the intensities of the vibrational bands when crystalline biphenyl melts or is dissolved [43-48]. On the other hand, the vibrational spectra of biphenyl or its deutero-analogues in solution or in the melt have been interpreted [32,49-52] on the assumption that the conformation is planar.

According to ultraviolet spectroscopic data, biphenyl has an intense (ϵ = 17 000–19 000) conjugation band near 250 nm, corresponding to the first $\pi-\pi^*$ electronic transition, which has been attributed both to the planar conformation [53-55] and to the fact that the angle between the fragments is appreciably less than 45° ($\lesssim$ 20°). [56-63] Measurements of the anisotropy of the electrical polarisability [64]

and diagmagnetic susceptibility [65] have led to the conclusion that the rings of the biphenyl molecule are located in the same plane in solutions.

The conformation of biphenyl in solution has been investigated in relation to biphenyl itself and its derivatives also using dipole moment [66] and light scattering [67-69] methods, electron paramagnetic resonance of the radical-anions [70,71], and NMR in the nematic phase [72]. Semi-empirical quantum-chemical calculations have been made of the conformation of biphenyl from its reactivity in nitration [73]. In some of these studies the dihedral angle between the planes of the rings was estimated as less than or equal to 30°, [66,68,69,71,72] while in others the closeness of the rings to the coplanar disposition was pointed out [67,70,73].

Thus theoretical and experimental studies (about 50 in all) on the conformations of biphenyl in solutions do not provide an unambiguous solution to the problem. However, as mentioned above, it has usually come to be assumed that biphenylylene systems and biphenyl itself are non-coplanar in solutions, like biphenyl in the gas phase, and the nature of their reactivities has been determined on this basis [1,2]. As will be shown below, this approach is unjustified, at least in relation to biphenyl.

III. STRUCTURAL FACTORS AND CONJUGATION IN BIPHENYL

Despite the fact that the ambiguity of the results of the determination of the conformation of biphenyl in solutions may be to some extent attributed to the very nature of the phenomenon (see, for example, Wilk [36]) a definite trend concerning the methods of investigation may be observed in the complete set of the available literature data. A planar or nearly planar conformation of biphenyl is indicated by methods involving the measurement of physical parameters about the direct dependence of which on conjugation (in this instance between the phenyl fragments) there is no doubt: the position and intensity of the long-wavelength absorption band in the ultraviolet spectrum [59a, 56], the anisotropy of the electrical polarisability of the molecules (the Kerr electro-optical effect [64]), and their diamagnetic susceptibility (the Cotton–Mouton effect [65]).

In biphenyl, which constitutes a weakly conjugated system comprising two aromatic rings [41,74], the conjugation depends on the angle between the planes of the rings and on the length of the central bond. As regards the relation between these two factors, until recently in theoretical studies the length of the bond between the rings was assumed to be constant for different angles of rotation or it was assumed that, as the angle between the planes of the rings increases, the degree of conjugation falls and there is a corresponding increase in the length of the bond [25,62,73,75]. However, experimental data indicate the opposite: as the biphenyl molecule ceases to be planar, i.e. when biphenyl passes from the crystalline to the vapour state, the length of the bond between the rings diminishes [12,13,17-19] approximately by 0.008–0.018 Å owing to the rapid decrease of the repulsive force between non-bonded atoms. This fact began to be taken into account very recently in quantum-chemical calculations on the biphenyl molecule [27,29,30], which is quite justified because the usual accuracy in the determination of the length of bonds between carbon atoms is to within 0.002 Å. [76]

So yet another cause of the contradictory results of the determination of the angle of twist of the central bond of biphenyl in solution become understandable. Methods where the degree of conjugation between the fragments is determined do not indicate or scarcely indicate the differences between the planar molecule (crystalline state) and the molecule in solution; there might be no difference, if, firstly, the conjugation were virtually independent of the type of conformation or, secondly, if under these and other conditions the molecule were planar. The second possibility must be rejected in the general case according to the results of studies by other methods. Thus careful analysis of the symmetry of the molecule on the basis of infrared and Raman spectra of biphenyl in the melt and in solutions, i.e. by methods which are not related to the conjugation between the rings, reveal a D_2 symmetry group or a non-polar conformation [39]; the same conclusion was reached by the authors of a number of other studies mentioned above. However, the first possibility remains.

Calculations have shown that the conjugation of the rings in biphenyl can indeed be independent of the angles between their planes when the latter are small (this is probable and is characteristic of biphenyl in solution). The ring conjugation energy found by different workers is 5–7 kcal mole^{-1}. [74] It is usually believed that this quantity is equal to the increase of the energy of the central bond owing to its π-component compared with the energy of a single bond between trigonal carbon atoms. When the rings rotate by an angle $\varphi = 30-45°$, the conjugation energy decreases in proportion to $\cos^2\varphi$, [77] i.e. by 1.5–3.0 kcal mole^{-1}. However, this would be true for a constant length of the central bond, whereas in reality the latter diminishes. The energy increment owing to the contraction of the bond may be estimated, for example, by employing the proportionality between the order and length of the bond, on the one hand, and between its order and its energy, on the other [78a,79]. More correct values should be obtained using Dewar and Schmeising's tractrix equation [80] for the relation between the length and energy of a bond of this kind. Similar ranges of values correspond to both methods of calculation: 1.8–3.9 and 1.5–3.4 kcal mole^{-1} respectively. In order to determine the increase in the energy of the π-component, it is necessary to introduce a correction for the change in the σ-component, which is positive or negative depending on what value is adopted for the equilibrium length of a "single" C_{sp^2}–C_{sp^2} bond—greater or smaller than in biphenyl. However, there is at present no definite answer to the question of the length of this bond: investigators have expressed divergent views and the range of probable values is 1.48 to 1.53 Å. [27,28,59c,78b,81b]. Nevertheless, if the correction to the change in the σ-component for different probable lengths of the σ-bond is calculated using the harmonic approximation to the Morse curve [82a], values not exceeding 0.3–0.6 kcal mole^{-1} are obtained; in our discussion they can be disregarded. A stabilisation energy of the π-component of the bond between the rings similar to the values obtained above, which is up to 3.0 kcal mole^{-1} and depends on the contraction of the bond, can be derived from the dependence of the "spectroscopic" resonance integral on the distance between the carbon atoms [59c].

We thus see that the decrease of the conjugation energy owing to the rotation of the biphenyl rings may be compensated by the simultaneous contraction of the bond between the rings, particularly if account is taken of the fact that the angle of rotation may be much less than 30 to 45° and a significant contraction of the bonds between the biphenyl ring should occur even when their angles of

rotation are small, owing to the rapid weakening of the nonbonding interactions in systems of this kind[27,59d].

The changes in the energy of the π-component of the bond can be set equal to the changes in the π-electron energy of the molecule[82b] and, if the latter are small or absent, then, for methods where the degree of conjugation is measured, the difference between the planar and slightly staggered molecular systems vanishes. One must therefore agree with the claim that the "estimation of the twist angles from ultraviolet spectra in such systems is extremely doubtful and risky, since... spectra calculated from the results of conformational analysis are almost independent of the twist angle"[83]. The phenomenon under discussion can thus be regarded as experimentally and theoretically well-founded.

This claim may not prove to be entirely correct, since in a number of studies[56-63] based on ultraviolet spectroscopic data small but significantly non-zero twist angles have been obtained for the central bond of biphenyl in solution, namely 18–23°. However, when the position of the first ultraviolet band of biphenyl in the spectra of solutions is compared with that in the spectra of the crystalline material, a correction must be applied for the "red shift" in the spectrum of the crystals. Its actual value for biphenyl is unknown and the arbitrary nature of the selection of such corrections[59e] virtually permits the assumption that the difference between the band positions is zero. If a small difference (1.5–3 nm or of 0.7–1.4 kcal mole^{-1}) between the energies of the $\pi-\pi^*$ transitions in both states remains even after the introduction of the correction, it may be caused by the distortion of the molecular skeleton of biphenyl in the crystal field[12-15], which should lead to a bathochromic shift of the conjugation band[59,84,85].

The extinction coefficient of the $\pi-\pi^*$ transition band in the biphenyl crystal cannot be determined owing to technical difficulties[57]. On the other hand, in the estimation of the angle of twist of the bond between the rings by comparing the extinction coefficients of this band in solutions of biphenyl and planar fluorene, the entire difference between them was attributed[56] solely to the non-coplanarity of the rings of the former. However, in the fluorene molecule the central bond is shorter than in biphenyl. This follows both from experimental data[86] and from a comparison of the results of semiempirical quantum-chemical calculations using the σ^*_{Ar} constants for the above compounds[87]. The greater intensity of the fluorene band may be caused in addition by the specific influence of the bridge group[88]. It is therefore of interest to note that biphenyl in solution exhibits a somewhat more intense conjugation band than 9,10-dihydrophenanthrene ($\varphi = 20°$ according to the model)[89].

Quantitative allowance for the above correction factors is extremely difficult or impossible. However, without it the instances of the application of ultraviolet spectroscopic methods to the conformational analysis of biphenyl can be used merely for the purpose of illustration.

The problem of the role of the conjugation between the rings in the study of the vibrational spectra of biphenyl is probably less well defined in view of the complexity of the interactions between the electronic and vibrational levels. The role of such conjugation varies as a function of the choice of particular bands and presumably the validity of the band assignment does not always guarantee the reliability of the final conclusions, because it is also not clear to what extent the crystalline state of the molecule may serve as an adequate model for the planar conformation. It is therefore difficult to give preference to the results of one study rather than another. Qualitative conclusions about the type of conformation based on the analysis of the symmetry of the molecule in solution are for this reason most significant.

IV. THE STRUCTURE AND REACTIVITY OF BIPHENYL IN SOLUTIONS

The foregoing considerations throw serious doubt on the validity of many postulates which have come to be widely held, namely:

(1) the low transmission coefficient of the *p*-biphenylylene system $\pi' = \rho_{p\text{-}C_6H_4C_6H_4}/\rho_{p\text{-}C_6H_4} \simeq 0.3$ can be accounted for by its non-coplanarity[2];

(2) the failure of biphenyl to obey the Selectivity Relations for the series of monosubstituted benzenes can be accounted for by the non-coplanary of its molecule[1];

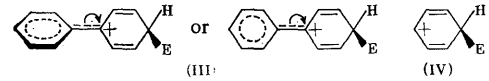
(3) the behaviour of fluorene as regards Selectivity Relations is different to that of biphenyl (a claim which aroused controversy at one time)[1,6,90];

(4) when account is taken of the activating influence of the bridge unit, the reactivity of fluorene in electrophilic substitution in the 2-position exceeds that of biphenyl in the 4-position owing to the non-coplanarity of the molecule of the latter[1].

Bearing in mind the considerations set out in the previous section, we shall examine these postulates in greater detail.

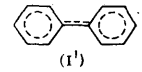
1. The low transmission coefficient π' of the biphenylylene molecular system (I) cannot be explained by its non-coplanarity, because the values of π' for the analogous fluorenylene system (II) are significantly the same[3,91]. We were unable to find any literature data on which a different claim could be based and were forced to conclude that the opposite views[2] are in all probability due to a misunderstanding.

2. The reactivity of biphenyl is higher than that of benzene owing to ring conjugation[92], which facilitates electron transfer to the reaction centre [ions (III) and (IV), *E* being an electrophile].



(III) (IV)

The conjugation effects are most important in highly selective reactions with large values of the constant ρ^+; according to modern views, the transition states in such reactions are structures closest to those of carbonium ion σ-complexes. For the most selective of the known reactions—molecular bromination ($\rho^+ = -12.1$)—the 4-position in biphenyl is more reactive than a single position in the benzene ring by a factor of 2920.[1] This is equivalent to a difference between the free energies of activation amounting to $\Delta\Delta F^{\neq} = (RT \lg 2920)/\lg e \simeq 5$ kcal mole^{-1}, which corresponds to the energy of conjugation via the central bond. The agreement in this instance is probably not fortuitous and this approach reveals an interesting aspect of the comparison of kinetic and thermodynamic (structural) factors in reactivity. The characteristic feature of the molecular structure of biphenyl (I')


(I')

namely that the bond between the rings (as well as the atoms involved in it) contributes a definite additional $\pi(p)$-electron density, is manifested by the corresponding

stabilisation of the transition state, which is evident from a comparison of ions (III) and (IV). In this approach there is no justification for postulating the inclusion of rotation and mutual approach of the rings in the reaction coordinate[1]. Evidently the conformational factor is immediately excluded from consideration if the initial state in solution involves a predominately planar conformation. The opposite case must in fact be considered.

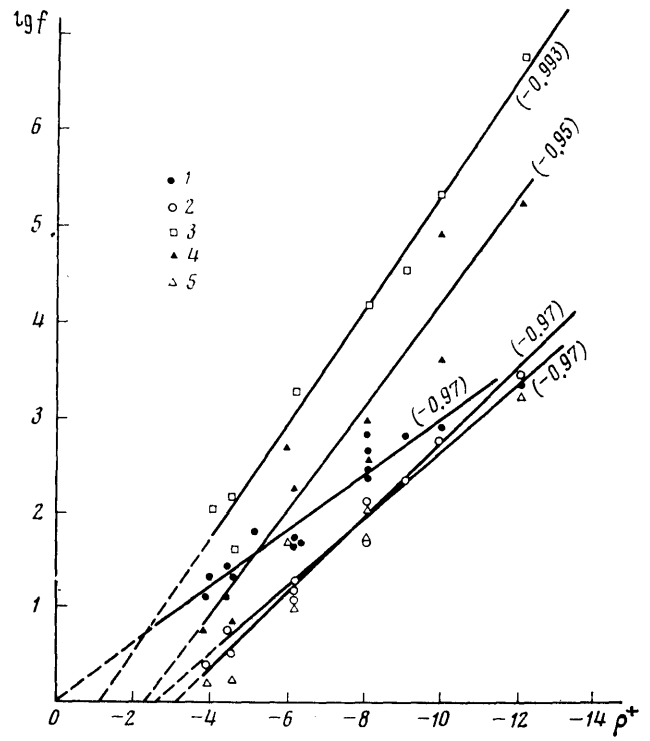
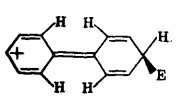


Figure 1. Dependence of the logarithms of the partial rate factors on ρ^+ in reactions with moderate and high selectivities[1] (the correlation coefficients are indicated in brackets): 1) *p*-tolyl; 2) 4-biphenylyl; 3) 2-fluorenyl; 4) 1-naphthyl; 5) 2-naphthyl.

Biphenyl does not obey Selectivity Relations for monosubstituted benzenes, which is evident from a comparison with toluene in Fig. 1. In reactions with moderate and high selectivities involving biphenyl the linear plot of $\lg f_{4\text{-Ph}}$ against ρ^+ (f is a partial rate factor) does not pass through the coordinate origin and has a higher slope than the analogous plot for toluene. In the most selective reaction (molecular bromination), the *para*-position in biphenyl is actually more reactive than in toluene. The explanation of these phenomena, involving the hypothetical carbonium ion (V)



(V)

as the model of the transition state, appears to be unlikely, as well as the claim that the degree of stabilisation of such an ion increases as a result of the contraction of the bond between the rings[1]. Indeed comparison of ion(V) not only with ion (III) but also with ion (IV) reveals that the formation of its structure requires an additional energy expenditure in order to disrupt the second aromatic π-electron sextet, to overcome the barrier to rotation, and to overcome increased non-bonded repulsions—in all about 60 kcal mole^{-1} (36 + 4 + 20 kcal mole^{-1} respectively; the non-bonding repulsion was estimated from known potential functions[28]). It is difficult to specify an energy source whereby such expenditure could be compensated. On the other hand, it is evident that a definite energy gain corresponds to structure (III).

The lower reactivity of biphenyl compared with toluene in the majority of reactions (Fig. 1) likewise need not be explained by the presence of an energy barrier to the rotation of the rings[1]. Using modern ideas about the transition state in electrophilic aromatic substitution as the product of the overall contribution of the σ- and π-complex structures[93,94], it is easy to find an acceptable explanation. For ionic or highly polar reactants (low values of ρ^+), the structure of the transition state is closer to that of π-complexes and the negative inductive effect of the phenyl substituent as well as the positive inductive effect of the methyl group begin to play an important role.

Thus, consideration of the reactivity of biphenyl does not require its molecular system to be coplanar in the transition state. Here it is important to know a significant fact—the equality of the entropies of activation for biphenyl, fluorene, and 9,10-dihydrophenanthrene in one of the most selective reactions—molecular chlorination[95]. Since biphenyl should possess some freedom of rotation of the rings about the central bond in solution (initial state), this finding does not support model (V) for the transition state.

The nature of the reactivity of biphenyl suggests that it can be only formally included among monosubstituted benzenes and that in essence it gravitates towards the group of polycyclic hydrocarbons (Figs. 1 and 2). Their distinctive features are a large size and conjugation of the π-electron systems. In general this creates better conditions for the delocalisation of the positive charge in the substitution step than in the usual benzene derivatives. The observed rates of highly selective reactions for compounds of this kind are much higher than would follow from the Selectivity Relations for monosubstituted benzenes. The foregoing is illustrated in Fig. 2 for the molecular chlorination and bromination reactions. A similar phenomenon has also been observed for the sulphonation of nitrobenzene with sulphuric acid ($\rho^+ = -10$).[99] Evidently the behaviour of biphenyl shows a greater similarity to that of fluorene, naphthalene, and other polycyclic hydrocarbons than to monosubstituted benzenes. It is striking that the reactivities of the 1- and 2-positions in naphthalene in relation to moderately selective reagents are several times lower than that of the *para*-position of toluene, whereas in the highly selective chlorination and bromination reactions naphthalene is more reactive than toluene by several orders of magnitude[1]. This finding can be explained, so far only qualitatively, on the basis of the same hypotheses as in the case of biphenyl.

3. One of the main pieces of evidence quoted by Stock and Brown[1] against Neuman's objection[6] to their conclusion that biphenyl and fluorene behave differently in electrophilic substitution is the, at first sight, greater variation of the $\sigma^+_{4\text{-Ph}}$ constants in various reactions compared

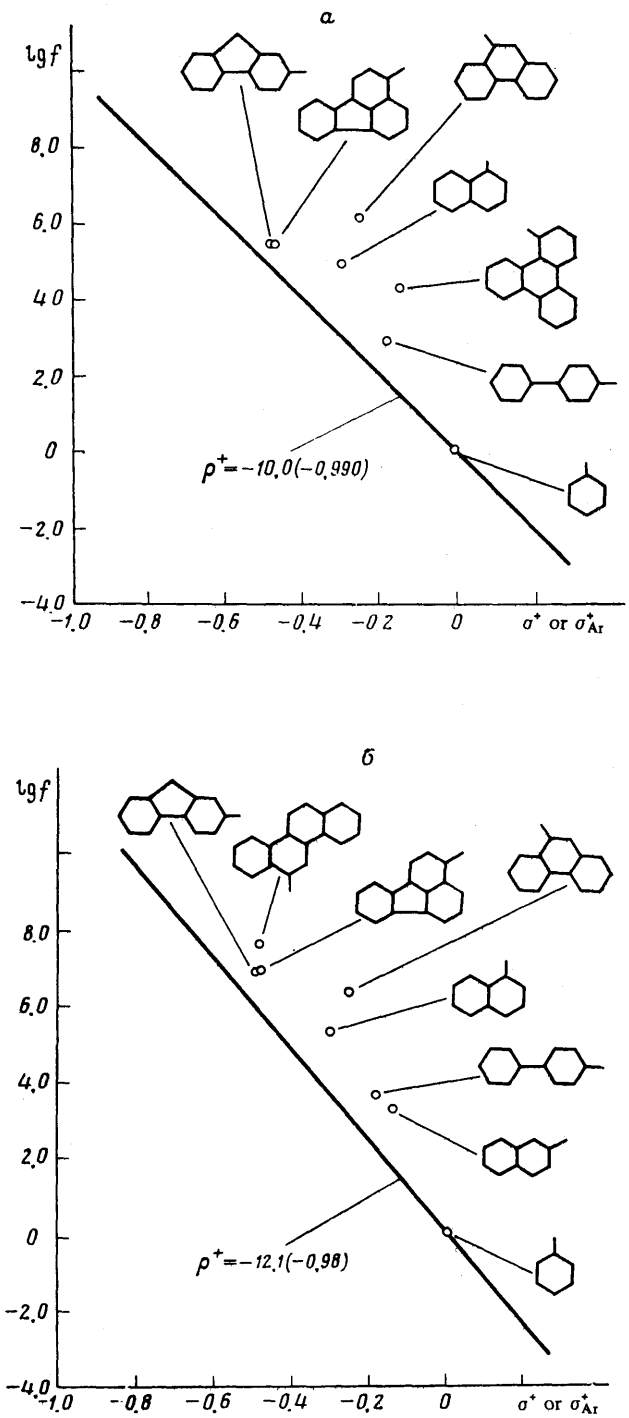


Figure 2. The Selectivity Relation for monosubstituted benzenes (straight lines) and for polycyclic hydrocarbons (circles): *a*) molecular chlorination in acetic acid[1,81b]; *b*) molecular bromination in acetic acid[1,96]. The values of σ^+_{Ar} were taken from Refs. 97–99 or calculated by Kachurin's method[99] from data quoted by Streitwieser[81c]; the correlation coefficients for monosubstituted benzenes are indicated in brackets.

with the $\sigma^+_{2\text{-Fl}}$ constants. However, the present author believes that in this case one can only speak of the variation of free energies, i.e. of the absolute and not relative variations of the constants. Fig. 3 clearly shows that the variation of the free energy of activation in the reactions of fluorene on average exceeds the corresponding variation for biphenyl. The problem of the causes of such variation is not the subject of the present review[99,100]. We shall also set aside the problem of the existence of a single scale of the Hammett–Brown constants for polycyclic hydrocarbons, applicable to all electrophilic substitution reactions. In view of the specific nature of polycyclic hydrocarbon systems, they cannot be accommodated within the same framework with monosubstituted benzenes. This fact is very likely to underlie the phenomenon under consideration.

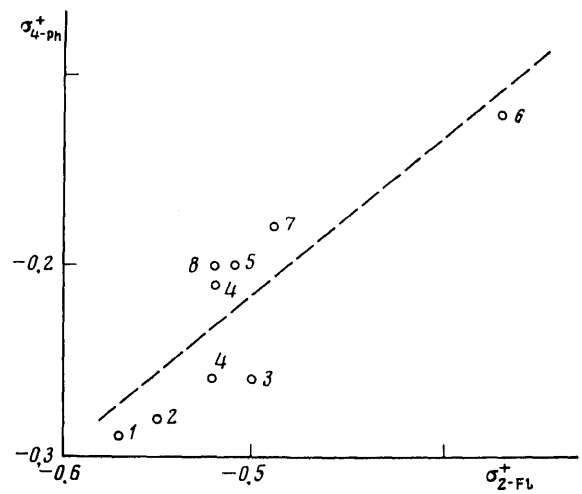


Figure 3. Variation of the constants $\sigma^+_{4\text{-Ph}}$ and $\sigma^+_{2\text{-Fl}}$ in various reactions[1] (the constants ρ^+ are indicated in brackets): 1) bromination (−12.1); 2) chlorination (−10.0); 3) acetylation (−9.1); 4) protodetritiation (−8.1); 5) nitration (−6.2); 6) protodesilylation (−4.6); 7) solvolysis of t-cumenyl chlorides (−4.5); 8) mercuration (−4.0); the slope of the dashed straight line is 0.83.

4. There is no need to resort to the conformational factor also in the treatment of the differences between the reactivities of fluorene and biphenyl. Compared with biphenyl, the bond between the rings in fluorene is shorter by 0.011–0.021 Å.[12,13,86] Using the average value 0.016 Å we find (see Section III) that it corresponds to an additional conjugation energy of 2.5 kcal mole^{-1} or to an acceleration of the highly selective reaction by a factor of ~ 70. If account is taken of the influence of the methylene bridge group[1], good agreement with experiment is achieved. This result is particularly interesting in view of the fact that quantum-chemical methods did not yield an interpretation of the reactivity of fluorene consistent with experiment and it was necessary to resort to the strained ring hypothesis[101–103].

Thus the characteristic behaviour of biphenyl in electrophilic substitution reactions can hardly be legitimately explained by the non-coplanarity of its molecule in solution.

Biphenyl is a special case of a substrate whose structure is intermediate between that of monosubstituted benzenes and polycyclic hydrocarbons. In contrast to the latter, the bond between the aromatic fragments of its molecule is appreciably weakened. The central bond is sometimes actually regarded as in essence a single bond[78c]. This fact is important for the understanding of the set of data known as the positive bridge effect, the conditions for the manifestation of which have been examined in a recent review[3].

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