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Reactivity and Transmission of Electronic Effects in Bridged Bicyclic Systems

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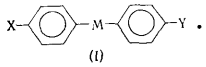
Analysis of data for the transmission of electronic effects in various biaryl systems has shown that the introduction of a bridge group between two benzene rings can both weaken and enhance the interaction between a substituent and a functional centre located in different rings. The nature and mechanisms of the enhanced transmission of electronic influences in bridged systems, called the positive bridge effect (PBE), have been examined and the principal conditions for the manifestation of PBE have been formulated.
The bibliography includes 192 references.

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I. INTRODUCTION

Extensive experimental data have now accumulated whose interpretation led to the discovery of certain general relations between the structure and properties of organic substances, which are very important for a quantitative theory of organic reactions[1-9]. The corresponding relations for benzene derivatives have been established from a large amount of data[1-6], but more complex systems have so far been inadequately studied. Investigation of aromatic compounds, which can be represented by structures of type (I), is of undoubted interest for the elucidation of quantitative relations governing the transmission of electronic effects in extended molecular systems:



(I)

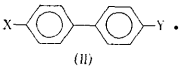
Here X is a substituent which influences the functional group Y and M is a bridge which consists either of a carbon-containing group ($-CH_2-$, $-CH_2-CH_2-$, $-CH=CH-$, $-C\equiv C-$, etc) or a heteroatomic unit (-O-, -S-, -Se-, -NH-, -N=N-, etc).

These compounds are now the subject of very comprehensive studies directed to the elucidation of both their detailed properties and the transmission of electronic effects in their molecules. Various chemical (determination of thermodynamic constants, kinetic measurements, and polarography) and physical (electron diffraction, ultraviolet, infrared, and Raman spectroscopy, NMR, and ESR) methods have been used for the solution of these problems. It is noteworthy that the experimental results themselves and their interpretation in various studies are sometimes contradictory. We therefore believe that it is extremely desirable to compare and discuss together the entire data concerned with the present problem.

It is important to note that compounds of type (I) are now used in a wide variety of fields of practical organic chemistry: in the manufacture of semiconductor materials[10], dyes[11], and physiologically active substances in pharmaceutical preparations[12-14], for the preparation of polymeric materials and their stabilisers[15,16], in the synthesis of reagents for analytical chemistry[17], etc.

II. THE BIPHENYL SYSTEM

The non-bridged biphenyl system (II) is interesting because it can serve as a standard for the comparison of transmission efficiencies in the series of bridged bicyclic systems (I).



(II)

When the problem of the reactivity of biphenyl derivatives was considered, it was initially assumed that the benzene rings act independently in the chemical sense: substituents in one ring do not influence the chemical reactivity of the other ring[18,19]. This conclusion was reached almost exclusively on the basis of the directing influence of substituents in biphenyl and its derivatives in electrophilic substitution reactions. However, this postulate was disproved by the results of Berliner and Blommers[20], who showed in a study of the dissociation of various derivatives of biphenyl-4-carboxylic acid that there is a relation, described by Hammett's equation, between the dissociation constant of the carboxy-group in one benzene ring and the electronic nature of the substituent in the other.

Systematic studies on the transmission efficiencies of biphenyl and other extended molecular systems have been made[21-32], the transmission efficiency being estimated from data for the reactions of the corresponding amines [Y = NH_2 in (I) and (II)] with *p*-nitrobenzoyl chloride (PNBC) and picryl chloride (PC) in benzene. These reactions are interesting because they are extremely sensitive to structural changes in the molecule of the amino-derivative (the ρ^0 for substituted anilines in the above reactions are respectively -3.10 [21,22] and -4.98[21,23,34]).

Table 1. Transmission coefficients in benzene and biphenyl systems.

No.	Reaction series[a]	$X-C_6H_4-Y$ standard ρ_{st}	System (II) ρ	System (II) π'
1	$ArCOOH \rightleftarrows ArCOO^- + H^+$; 20°, 50% butylcellosolve-water[20,35]	1.32	0.49	0.37
2	$ArCOOH \rightleftarrows ArCOO^- + H^+$; 25°, H_2O[36]	1.00	0.32	0.32
3	$ArCOOH \rightleftarrows ArCOO^- + H^+$; 25°, 50% EtOH — H_2O[36]	1.69	0.48	0.28
4	$ArCOOEt + OH^- \rightarrow ArCOO^- + EtOH$; 25°, 88% EtOH — H_2O[37]	2.57	0.62	0.24
5	$ArCOOH + Ph_2CN_2 \rightarrow ArCOOCHPh_2 + N_2$; 30°, EtOH[38]	0.95	0.22	0.24
6	$ArNH_2 + 2,4,6\text{-}(NO_2)_3C_6H_2Cl \rightarrow 2,4,6\text{-}(NO_2)_3C_6H_2NHAr + HCl$; 25°, C_6H_6[31,33,34]	−4.98	−1.56	0.31
7	$ArC_6H_4NH_2 + 2,4,6\text{-}(NO_2)_3C_6H_2Cl \rightarrow 2,4,6\text{-}(NO_2)_3C_6H_2NHC_6H_4Ar + HCl$; 25°, C_6H_6[31,34]	−1.56	−0.49	0.31[b]
8	$ArNH_2 + C_6H_5COCl \rightarrow C_6H_5CONHAr + HCl$; 25°, C_6H_6[31,39,40]	−3.23	−1.07	0.33
9	$ArNH_2 + 4\text{-}NO_2C_6H_4COCl \rightarrow 4\text{-}NO_2C_6H_4CONHAr + HCl$; 25°, C_6H_6[22]	−3.10	−1.40	0.45
10	$ArNH_2 + 4\text{-}NO_2C_6H_4SO_2Br \rightarrow 4\text{-}NO_2C_6H_4SO_2NHAr + HBr$; 25°, $C_6H_5NO_2$[41,42]	−3.82	−1.44	0.38
11	$Ar\overset{+}{N}H_3 \rightleftarrows ArNH_2 + H^+$; 25°, H_2O[43,44]	2.60	0.89	0.34
12	$Ar\overset{+}{N}H_3 \rightleftarrows ArNH_2 + H^+$; 20°, 50% EtOH — H_2O[35]	−3.00	−0.72	0.24
13	$ArOH \rightleftarrows ArO^- + H^+$; 20°, H_2O[45]	2.11	0.62[c]	0.29
14	$ArSi(CH_3)_3 + H_2O \rightarrow ArH + (CH_3)_3SiOH$; 50°, $CH_3COOH - H_2SO_4$[46]	−4.35	−1.33	0.30
15	$ArCOCH_3 + C_2H_5OD \rightleftarrows ArCOCH_2D + C_2H_5OH$; 20°, EtOH[47]	1.60	0.40	0.25
16	$ArOH \rightleftarrows ArO^- + H^+$; 20°, 60% dioxan-water[48,49]	2.81	0.76	0.27
17	$ArOH \rightleftarrows ArO^- + H^+$; 20°, 60% EtOH — H_2O[49]	2.88	0.81	0.28
18	$ArOH \leftrightarrows ArO^- + H^+$; 20°, 60% acetone-water[50]	2.67	0.99	0.37
		π'_{av}	0.31±0.01	

[a]Here and henceforth the reactions of compounds Ar − Y are considered, Ar being groups corresponding to various derivatives of the standard and given systems (in the present instance $X-C_6H_4$ and $X-C_6H_4-C_6H_4$). [b]The coefficient π' was calculated for the *p*-terphenyl system relative to the biphenyl system. [c]Determined from two points for X = H and NO_2.

The constants ρ for various reactions involving biphenyl derivatives are presented in Table 1, which includes for comparison the analogous quantities for similar reactions of benzene derivatives. Comparison of the results makes it possible to estimate the transmission efficiency of the system as its length is increased by one benzene ring. The coefficient of transmission of electronic effects $\pi' = \rho/\rho_{st}$ (or ρ^0/ρ^0_{st}), where $\rho(\rho^0)$ is the transmission efficiency in the given system and $\rho_{st}(\rho^0_{st})$ the transmission efficiency in the standard system, is used to characterise quantitatively the above change. It was found that regardless of the nature of the reaction series and its sensitivity to the influence of the substituents (the values of ρ for benzene derivatives vary in the range from +2.88 to −4.98), the second benzene ring invariably decreases the effectiveness of the substituent approximately by a factor of three ($\pi'_{av} = 0.31 \pm 0.01$). A similar change in the transmission of electronic effects has been observed also following the introduction of a third benzene ring (on passing from biphenyl to terphenyl; Table 1, No. 7).

The steric structure of the system can influence significantly its transmission efficiency. A convincing illustration of this is provided by the study of the reactivity of compound (II) with Y = NH_2, containing in addition two pairs of permanent substituents in the 3,3′- and 2,2′-positions (reactions with PNBC in benzene at 50°C)[22,23,25-30]. 3,3′-Substituents are known to have little influence on the steric disposition of the benzene rings in biphenyl[52-54] and $\rho = -1.30$ is therefore found to be almost equal to that for system (II) ($\rho = -1.34$). On the other hand, the introduction of 2,2′-substituents of different types increases the dihedral angle φ (the angle between the planes of the benzene rings) from 35–40°[55-59] to about 90°[52-54], which decreases the transmission of effects in the biphenyl system containing 2,2′-substituents such as Cl, Br, CH_3, CH_3OCO, and i-C_3H_7OCO approximately by a factor of 1.5 ($\rho \simeq 0.92$). A similar result was obtained also for the introduction of a single bulky substituent in the 2-position, as shown by the basicities of 4-aminobiphenyl ($\rho^0 = -0.52$) and 4′-amino-*o*-terphenyl ($\rho^0 = -0.35$†)[60] derivatives in 50% aqueous ethanol at 20°C.

A study of the same reaction of similar aminofluorene derivatives [Y = NH_2 in (II); the 2,2′-positions are linked by methylene units], where the system is coplanar, showed that the transmission efficiency ($\rho = -1.65$) is in this case only 20% higher than in compounds of this type (II)[22,29]. This suggests that the increased planarity of the system entails hardly any increase in its transmission efficiency, since on taking into account the second pathway for the transmission of effects (via the methylene unit) one would expect an increase of ρ approximately by 50% (see the transmission efficiency of diphenylmethane‡ in Table 2). The insignificant influence of the coplanarity of the benzene rings in the fluorene system on the transmission of electronic effects is indicated also by other data[45,46,61].

Apart from the above investigations, undertaken to estimate the transmission of electronic effects via the molecular system of (II) from reactivity data (Table 1), there have also been studies where attempts were made to solve the above problem with the aid of, for example,

†We calculated ρ^0 from the literature values[60] using $\sigma^0_{p\text{-}NO_2} = 0.73$.

‡It is assumed to a first approximation that the transmission efficiencies of the 3,3′- and 4,4′-diphenylmethane systems are approximately the same.

measurements of dipole moments, polarographic reduction (oxidation) half-wave potentials, and ESR, NMR, ultraviolet, and infrared spectra of the corresponding compounds.

Comparison of the dipole moments of 4- and 4,4′-substituted biphenyls revealed[62-64] that there is an appreciable interaction between substituents of different electronic types, which is somewhat reduced compared with the corresponding interaction in benzene. However, it is fairly difficult to estimate quantitatively this weakening from the results of the above studies owing to the difficulty of allowing for different kinds of structural factors (configuration of the system, distance between the substituents), which influence the measured dipole moments. This is even more difficult in systems (I) which will be considered below. Therefore in the present review we shall not deal with these investigations in detail.

The study of the polarographic reduction of various 3′- and 4′-derivatives of 4-nitrobiphenyl to the corresponding radical-anions[65,66] and of their ESR spectra showed that the influence of substituents on their first half-wave potential ($E_{1/2}$) and on their spin densities is satisfactorily consistent with the Hammett equation. Comparison with the analogous results for nitrobenzene derivatives indicates a decreased transmission of electronic effects in the bicyclic system compared with the monocyclic system. A similar conclusion was reached also in a study of the polarographic reduction of a number of 4′-derivatives of 4-acetylbiphenyl.[67] However, we believe that data of this kind should be treated with caution, since it is not altogether clear to what extent the quantity ρ can characterise in this case the transmission efficiency of the system. The point is that in polarographic reduction the electron enters the first vacant orbital of the entire molecule and is only then localised in a particular fragment of the latter. For this reason, the system as a whole must be considered as the reaction centre[68,71]. Therefore the experimental results for the polarographic reduction (oxidation) as well as the ESR spectra of substituted biphenyls probably do not characterise unambiguously§ their ability to transmit electronic effects.

To the same extent the above considerations apply also to the electronic spectra of the compounds. Although numerous studies have been made of the spectra of biphenyl and its various derivatives[72-76], one may conclude on their basis only whether or not there is conjugation between the fragments of the system but nothing can be inferred about the nature of the transmission of electronic effects through the system.

On the other hand, the study of both infrared and NMR spectra, where the "reaction centre" is clearly revealed, makes it possible, in principle, to derive definite information about the transmission of electronic effects in such systems. Indeed it has been established from the N–H stretching vibration frequencies in (II) (Y = NH_2)[43] that the biphenyl system transmits such influences much less effectively than the benzene system. The coefficients π', calculated from the shift of the absorption band maxima corresponding to the symmetric (ν_S) and asymmetric (ν_{as}) stretching vibrations, are 0.31 and 0.37 respectively, i.e. close to the values listed in Table 1. Unfortunately the accuracy of the above investigation is not always very high as yet, so that the experimental errors are sometimes comparable to the measured quantities. For example, in a study of the stretching vibration frequencies of the NO_2 group it was found that the difference $\Delta\nu$ between the wavenumbers of 4-nitrobiphenyl and its 4,4′-dinitro-analogue is only 1 cm^{-1}, which is actually less than the error in the determination of the wavenumbers (usually to within 2 cm^{-1}).[77] Because of this, the choice of a functional group sufficiently sensitive to the substitution is an important problem in such studies[43], since the reliability of the results depends significantly on it. Hence it follows that not all the investigations of infrared spectra are of equal value for a quantitative determination of the transmission efficiencies of the systems considered.

Comparison of the NMR spectra of a series of different benzene and biphenyl derivatives shows quite clearly the attenuating effect of the second benzene ring. This, according to ^1H NMR, this influence for the OH group in phenol derivatives (ρ = 1.54)[78,79] and 4-hydroxybiphenyl derivatives (ρ = 0.712)[80] is reflected by the value π' = 0.46. On the other hand, it is difficult to determine unambiguously the coefficient of transmission of electronic effects through the second benzene ring from the ^{19}F chemical shifts δ for the corresponding derivatives. The point is that the influence of the 4′-substituent is in this case described by the two-parameter equation[81-84]

$$\Delta\delta = \rho_I\sigma_I + \rho_R\sigma_R. \qquad (1)$$

The relation between the constants ρ_I and ρ_R, characterising the sensitivity of a series of compounds to the inductive and conjugation effects of substituents, changes on passing from one series to another. Therefore it is necessary to calculate separately the values of π' for the inductive and resonance effects on the basis of data of this kind[85-87]. It was found that the inductive transmission of effects through the second benzene ring in system (II) (π'_I) changes from 0.50 (in cyclohexane) to 0.33 (in dimethyl sulphoxide). The transmission coefficient of this ring π'_R, estimated from the ρ_R, is almost independent of the solvent and amounts to 0.15.

Thus NMR data (and in many cases infrared spectroscopic data) for benzene and biphenyl derivatives show that, on passing from the former systems to the latter, there is an appreciable weakening of the interaction between the substituent and the functional centre. This weakening is approximately equal to that found from the results of other studies (Table 1). However, there is one factor which somewhat restricts the application of spectroscopic data in a quantitative estimation of the transmission efficiency of extended molecular systems. The sensitivity of the reaction series to the influence of substituents is usually determined by comparing the measured quantities with σ constants. The latter characterise in essence[1-8] the differences between the effects of the substituent on the initial and final (or transition) states of the reaction centre. Therefore, despite the large number of successful applications (Zhdanov and Minkin[6], Chapter VII), the problem of a direct comparison of σ constants with spectroscopic data characterising only one (initial, final, or excited) state of the functional centre still remains open[84,88].

Bearing in mind all the foregoing considerations, we shall concentrate attention primarily on the results obtained in the study of equilibria or reaction rates and those of other investigations will be quoted only whenever convenient.

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§The complexity of the situation can be illustrated, for example, by the following fact. Two straight lines with different slopes and separated by an appreciable distance have been obtained[65,66] on the $E_{1/2}$–σ correlation graph for 4′-substituted derivatives of 4-nitrobiphenyl.

Table 2. Transmission coefficients in systems (I) with saturated hydrocarbon bridges.

No.	Reaction series	System (II)	M = $-CH_2-$ in (I)		M = $-CH_2-CH_2-$ in (I)	
		ρ^0_{st}	ρ^0	π'	ρ^0	π'
1	$ArNH_2 + 2,4,6\text{-}(NO_2)_3C_6H_2Cl \rightarrow 2,4,6\text{-}(NO_2)_3C_6H_2NHAr + HCl$; 25°, C_6H_6[21,89]	−1.56	−0.95	0.61	−0.71[a]	0.46
2	$ArNH_2 + 4\text{-}NO_2C_6H_4COCl \rightarrow 4\text{-}NO_2C_6H_4CONHAr + HCl$; 25°, C_6H_6[21,22,89]	−1.40	−0.87[a]	0.62	—	—
3	$ArNH_2 + 4\text{-}NO_2C_6H_4SO_2Br \rightarrow 4\text{-}NO_2C_6H_4SO_2NHAr + HBr$; 25°, $C_6H_5NO_2$[41]	−1.44	−0.39	0.27	—	—
4	$ArNH_2 + C_6H_5COCl \rightarrow C_6H_5CONHAr + HCl$; 25°, C_6H_6[22,90–92]	−1.07	−0.48[b]	0.45	—	—
5	$ArNH_3 \leftrightarrows ArNH_2 + H^+$; 25°, H_2O[43]	−0.89	−0.65	0.73	—	—
6	$HON_2ArN_2OH \leftrightarrows HON_2ArN_2O^- + H^+ \leftrightarrows 2H^+ + {}^-ON_2ArN_2O^-$; 18°, H_2O[93]	−1.70[c]	−0.80[c]	0.47	−0.60[c]	0.35
		π'_{av}	0.53±0.06		0.40±0.06	

[a, b] Determined from two points for X = H and NO_2 (a) or H and NH_2 (b). [c] The difference $pK_1 - pK_2$, proportional to ρ, is quoted, since ρ cannot be calculated owing to the lack of the values of σ for the 4′-N_2OH^+ and 4′-N_2O groups.

III. SYSTEMS WITH CARBON-CONTAINING BRIDGE GROUPS

The entire data referring to the transmission efficiency of bicyclic systems with carbon-containing bridges can be usefully divided into two conventional groups. One of these includes systems with bridges consisting of saturated hydrocarbon units and the other systems with bridges incorporating multiple bonds.

1. Saturated Groups

The results of studies of the transmission of electronic effects in diphenylmethane and bibenzyl systems, where the benzene rings are separated by $-CH_2-$ and $-CH_2-CH_2-$ groups, are presented in Table 2, which includes also the coefficients π' calculated for them relative to system (II), which clearly indicate the insulating role of the hydrocarbon units. The transmission coefficient of the methylene unit in diphenylmethane (0.53 or 0.58 if the extremely low value of π' for series No. 3 is excluded) proved to be somewhat higher than in aliphatic systems (0.350, [94] 0.360, [3] and 0.388 [7]). This may be due to some involvement of the σ, π conjugation of the C–H bonds of the methylene unit with the benzene rings [32,95]. However, one should bear in mind that, when the capacity of the methylene unit for the inductive transmission of electronic effects ($Z^*_{CH_2}$) is estimated from data for aliphatic compounds where the amino-group is the reactive centre (as in the majority of the series in Table 2), the coefficient increases to 0.470–0.554 [94,96,97] and becomes almost equal to π'_{av} in Table 2. The observed transmission efficiency of a single methylene unit in bibenzyl hardly differs from that in the diphenylmethane system.

The compounds considered were also investigated by other methods. The available ultraviolet spectroscopic [98–100], ESR, and polarographic [101,102] data indicate the insulating effect of the methylene units in these systems. However, for the reasons stated, such data can only yield a qualitatitive idea about the properties of these compounds in which we are interested. As regards the estimation of the transmission of electronic effects in these compounds from infrared spectra, there is a full analogy¶, as for benzene and biphenyl derivatives, with the results obtained in studies on the reactivity of the compounds [43].

The values of π' for M = $-CH_2-$ in Table 2 agree with those determined from NMR data for a series of diphenylmethane derivatives (Y = ^{19}F) [86,87,103]. Thus the coefficients π' for M = $-CH_2-$, $-CHPh-$, $-CH(OH)-$, $-CCH_3(OH)-$, $-CPh(OH)-$, and $-CCF_3(OH)-$, calculated from the ρ_I, are in the range from 0.41 to 0.55 and those calculated from the ρ_R are between 0.34 and 0.50. But, when the transmission coefficient is estimated by a direct comparison of the chemical shifts in the spectra of compounds (I) and (II), then it is found to be in the range from 0.30 to 0.62 for systems of this kind. On the other hand, $\pi' = 0.18$, determined from NMR spectra (Y = ^{19}F) [87] for the two-unit bridge group $-CH_2-CH_2-$, proved to be much lower than the value in Table 2.

2. Groups Containing Multiple Bonds

The transmission coefficients π' for bicyclic systems with unsaturated bridge units such as $-C\equiv C-$, $-CH=CH-$, $-CH=\overset{+}{N}-$, $-N=CH-$, $-N=N-$, $-C_6H_4-$, $-CH=\overset{+}{N}(CH_3)-$, and $-\overset{+}{N}(CH_3)=CH-$ (the reaction centre is to the right of the bridge and the substituent is to the left) are compiled† in Table 3.

Comparison of these data leads to the conclusion that any uncharged two-unit bridge with a multiple bond reduces the ability of the system to transmit electronic effects approximately by a factor of 1.7. Bridges containing only carbon atoms behave in almost exactly the same way as those consisting of one or even two heteroatoms (cf. the coefficients π' for the $-CH=CH-$, $-CH=N-$, $-N=CH-$, and $-N=N-$ bridges).

It is interesting that, on passing from bibenzyl, where there is a two-unit $-CH_2-CH_2-$ bridge (Table 2), to the stilbene and tolane systems, where M = $-CH=CH-$ and $-C\equiv C-$ respectively (Table 3), the influence of the substituents increases only by a factor of 1.5, although the last two compounds represent a classical instance of π, π conjugation of multiple bonds, which is interrupted in bibenzyl by the saturated bridge group.

As regards the ability to transmit electronic effects, the stilbene and tolane systems (Table 3) hardly differ

¶Data [77] where the nitro-group is used as the functional centre constitute the only exception. Here it is almost impossible to reach any conclusions owing to the low sensitivity of this centre to the effect of the substituent [43].

†The azobenzene system, which has no carbon atoms in the bridge, is considered here in view of its structural similarity to stilbene.

Table 3. Transmission coefficients in systems (I) with bridges M containing multiple bonds.

No.	Reaction series	System (II)	M=—C≡C—		M=—CH=CH—		M=—CH=N—		M=—N=CH—		M=—N=N—		M=—C_6H_4—		M=—CH=$\overset{+}{N}(CH_3)$—		M=—$\overset{+}{N}(CH_3)$=CH—	
		ρ_{st}	ρ^0	π'	ρ^0	π'	ρ	π'	ρ	π'	ρ	π'	ρ^0	π'	ρ	π'	ρ	π'
1	$ArNH_2$ + 2,4,6-$(NO_2)_3C_6H_2Cl$ → → 2,4,6-$(NO_2)_3C_6H_2NHAr$ + HCl; 25°, C_6H_6[31,104—106]	—1.55	—0.91[a]	0.59	—0.97[a]	0.62	—	—	—	—	—1.20[a]	0.77	—0.49[a]	0.31	—	—	—	—
2	$ArNH_2$ + 4-$NO_2C_6H_4COCl$ → HCl + + 4-$NO_2C_6H_4CONHAr$; 25°, C_6H_6[22,104—106]	—1.40	—0.83	0.59	—0.94[a]	0.67	—	—	--	—	—0.98[a]	0.70	—	—	—	—	—	—
3	$Ar\overset{+}{N}H_3 \rightleftarrows ArNH_2 + H^+$; 25°, H_2O[43]	0.89	—	—	0.52[a]	0.58	—	—	—	—	—	—	—	—	—	—	—	—
4	$Ar\overset{+}{N}H_3 \rightleftarrows ArNH_2 + H^+$; 20°, 50% EtOH—$H_2O$[107—109]	0.72	—	—	0.42	0.59	—	—	—	—	0.36	0.50	—	—	—	—	—	—
5	$Ar\overset{+}{N}H(CH_3)_2 \rightleftarrows ArN(CH_3)_2 + H^+$; 20°, 50% EtOH—$H_2O$ [2] (Zhdanov and Minkin[6], p.59)	1.20[b]	—	—	0.52[c]	0.43	—	—	—	—	0.53	0.44	—	—	—	—	—	—
6	$ArOH \rightleftarrows ArO^- + H^+$; 25°, 98% MeOH—$H_2O$[110,111]	0.60[b]	—	—	—	—	0.30	0.49	0.37	0.61	—	—	—	—	1.17	1.94	1.95	3.23
7	$HON_2ArN_2OH \rightleftarrows HON_2ArN_2O^- + H^+ \rightleftarrows \rightleftarrows 2H^+ + {}^-ON_2ArN_2O^-$; 18°, H_2O[93]	—1.70[d]	—	—	—1.10[d]	0.64	—	—	—	—	—	—	—	—	—	—	—	—
8	$ArCOOH \rightleftarrows ArCOO^- + H^+$; 25°, 98% MeOH—$H_2O$[111]	0.45[b]	—	—	—	—	—	—	0.28	0.62								
		π'_{av}	0.59		0.59±0.03		0.49		0.62		0.59±0.06		0.31		1.94		3.23	

[a]Determined from two points for X = H and NO_2. [b]ρ_{st} estimated from the values of ρ for benzene derivatives and the coefficient π'_{av} in Table 1. [c]Since the —CH=C(CN)— group is the bridge, this result was disregarded in the calculation of π'_{av}. [d]The difference $pK_1 - pK_2$ is quoted (see footnote c to Table 2).

quantitatively from the diphenylmethane system (Table 2). On this basis, one may conclude that the familiar rule of vinylogy, according to which the electronic influence of the substituent in conjugated systems is transmitted to the reaction centre without appreciable decay (Reutov[112], p. 85) is not confirmed in quantitative studies on this problem (at least in a series of molecular systems resembling those described). This is apparently caused by the decisive role of the inductive mechanism in the transmission of electronic effects in systems of this kind.

When the structure of tolane is compared with those of stilbene and biphenyl, then, in contrast to stilbene which has a *trans*-configuration and a non-coplanar structure[113—116] and in contrast to biphenyl where the hydrogen atoms in the 2,2′-positions hinder the rotation of the benzene ring about the single bond joining them[56—58,117], the tolane system offers the smallest steric hindrance to the electronic interaction between the benzene rings on either side of the acetylene bridge, owing to its linearity and the appreciable distance between the 2,2′-hydrogen atoms[118]. However, this interaction is less pronounced in tolane than in the biphenyl system and is the same as in stilbene. This is most probably due to the fact that the carbon—carbon triple bond in organic molecules has no particular advantages over a similar double bond as regards transmission of electronic effects, despite its greater degree of unsaturation and shorter length.

The coefficient π' for system (I) with M = $-C_6H_4-$ (the *p*-terphenyl system) (Table 3) has the smallest value (0.31), which is consistent with the greatest length of the above bridge. As already mentioned, it is equal to π' for the biphenyl system relative to the benzene system (Table 1).

Data on the transmission of electronic effects in a series of bicyclic systems containing the charged bridges $-\overset{+}{N}(CH_3)=CH-$ and $-CH=\overset{+}{N}(CH_3)-$ (Table 3) require special consideration. Here the π' are significantly greater than unity (1.94 and 3.23 respectively), while the transmission coefficients for the analogous uncharged bridges —CH=N— and —N=CH— are small and virtually equal to the values for other diatomic bridges with a double bond (Table 3). The sharp increase in the transmission efficiency of azomethine bridges following the quaternisation of their nitrogen (by a factor of 4—5) was initially explained[110,111] by a transition from the non-coplanar structure of the Schiff bases, due to the competing interaction of the π electrons of one of the benzene rings both with the double bond and with the lone electron pair of the nitrogen[119—122], to the coplanar structure in the case of the charged bridges, where the above competition does not occur and the benzene ring is conjugated only with the double bond. However, this fact hardly plays a decisive role because in the stilbene, tolane, and azobenzene systems, where the conditions for conjugation are better than in the systems considered here (in the latter there is no steric interaction of the *N*-methyl group with the *ortho*-hydrogen atoms of the benzene ring), the transmission efficiency is virtually the same as in the benzylidene anil systems (cf. the values of π' in Table 3).

The enhancement of the electronic interaction of the substituent with the reaction centre in systems (I) containing unsaturated two-unit bridges relative to system (II) was also observed by Frankovskii and coworkers, who investigated the acidity of the corresponding phenol derivatives (Table 4).

The phenomenon of enhanced transmission efficiency ($\pi' > 1.0$) was observed for the first time in a study of bicyclic systems containing bridge heteroatoms (see the next Section). We shall therefore return somewhat later to the explanation of the "anomalously" high transmission efficiency (Tables 3 and 4). However, here one should note that the introduction of substituents (OH or Cl) into phenol derivatives (Table 4) in the 2- or 2′-position relative to the bridge unit, which influence the steric structure of these compounds, leads to an increase of transmission efficiency. This is manifested particularly

clearly in derivatives of 2,4-dihydroxyazobenzene, where the system becomes more coplanar as a result of the formation of an intramolecular hydrogen bond[50,124,125] and yet another pathway for the transmission of the influence of the substituent on the activity of the reaction centre appears:

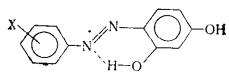


Table 4. Transmission coefficients in the azobenzene system [R and R′ are the substituents in X – (2′-R′) $-C_6H_3-N=N-C_6H_3-$(2-R)–OH-4].

No.	Reaction series	System (II)	R=R′=H		R=H, R′=Cl		R=OH, R′=H	
		ρ_{st}	ρ	π'	ρ	π'	ρ	π'
1	ArOH ⇄ ArO^- + H^+; 20°, 60% EtOH–H_2O [48,49,123–125]	0.81	0.84	1.03	0.93	1.15	2.18	2.68
2	ArOH ⇄ ArO^- + H^+; 20°, 60% dioxan-water [48,49,123,124]	0.76	0.93	1.22	0.98	1.28	1.89	2.48
3	ArOH ⇄ ArO^- + H^+; 20°, 60% acetone-water [50]	0.99	0.91	0.92			2.28	2.31
		π'_{av}	1.06±0.09		1.22±0.07		2.49±0.12	

It is interesting to compare the transmission efficiency data in Tables 3 and 4 with the results obtained in studies of the NMR spectra of a series of analogous compounds.

Table 5. Transmission coefficients estimated with the aid of NMR for systems (I) with bridges containing multiple bonds

No.	Bridge M in (I)	Y=^{19}F [86,103]			Y=^{19}F [87]	Y=OH [50,80]
		π'_I	π'_R	n^a	π'	π'
1	—CH=CH—	0.67±0.02	0.67±0.01	6	0.74[b]	—
2	—N=CH—	0.63±0.01	0.68±0.01	9	—	—
3	—CH=N—	0.63±0.02	0.64±0.01	9	—	—
4	—N=N—	0.91±0.02	0.88±0.01	3	—	0.60[c]
5	$-CH=\overset{+}{N}H-$	1.08[d]	0.62[d]	1	—	—
6	$-\overset{+}{N}H=CH-$	1.47[d]	0.98[d]	1	—	—

[a]The number of solvents in which compounds of types (I) and (II) were investigated (average values of π' are quoted for $n > 1$). [b]Estimated by a direct comparison of the values of Δδ. [c]The chemical shift of the hydroxyl protons were measured and compared. [d]Measurements for compounds of types (I) and (II) were made in FSO_3H and CH_3OH respectively.

Table 5 shows that the transmission efficiency of the system with the –N=N– bridge (No. 4), which has been estimated from the chemical shifts of the hydroxyl protons, agrees well with the efficiency determined from different chemical data (Table 3). On the other hand, the ability of the above bridge to transmit electronic effects determined from the ^{19}F chemical shifts proved to be higher by a factor of 1.5 and its value approached that in Table 4. Hence it follows that the transmission efficiency of the bridge system depends significantly on the nature of the functional centre. The reasons for this will be discussed a little later.

Comparison of the data in Table 5 for the transmission efficiencies of systems (I) with different bridge units, estimated with the aid of the π'_I (for Y = ^{19}F), leads to the conclusion that the efficiency increases steadily on passing from the –CH=CH–, –CH=N–, and –N=CH– bridges, where it does not differ significantly from the value determined for other reaction series (Table 3), to the –N=N–, $-CH=\overset{+}{N}H-$, and $-\overset{+}{N}H=CH-$ bridges. The series based on the transmission efficiency (the bridges are indicated) $-\overset{+}{C}H=CH- \simeq -CH=N- \simeq -N=CH- < -N=N- < -CH=\overset{+}{N}- < =\overset{+}{N}-CH-$ agrees well with the series found from the dissociation data for the corresponding hydroxy-derivatives (No. 6 in Table 3 and Table 4).

IV. SYSTEMS WITH BRIDGE HETEROATOMS CAPABLE OF ELECTRON DONOR CONJUGATION

1. The Positive Bridge Effect (PBE)

In studies on the transmission of electronic effects in a series of systems (I) with bridge heteroatoms on the basis of acylation reactions of the corresponding amino-derivatives (Y = NH_2), the above property was initially estimated in terms of the value of f, [21,126] which is equal to the ratio of the rate constants for the unsubstituted amine and its nitro-derivative (X = H or NO_2). The results (Table 6) show that the introduction of a bridge heteroatom with lone electron pairs between two benzene rings (Nos. 2–5) can not only weaken the electron influence of the substituent on the functional activity of the reaction centre relative to the biphenyl system without a bridge (No. 1) but can also significantly increase it. This phenomenon has been called the positive bridge effect (PBE)[129].

Table 6. The factors f (at 25°C) and ΔpK_a for systems (I) with bridge heteroatoms.

No.	Bridge M in (I)	f_{PNBC}*	f_{PC}	ΔpK_a [48]
1	— (biphenyl)	10.6[31]	13.6[22]	0.54[a]
2	—O—	12.1[127]	15.8[127]	—
3	—S—	23.8[128]	30.7[128]	0.81[a]
4	—Se—	—	24.7[21]	—
5	—NH—	—	43.3[106]	0.82[a]

[a]The difference for X = H and NO_2 is quoted.

*p-nitrobenzoyl chloride (Ed. of Translation).

The first publications dealing with the manifestation of PBE [21,126,129,130] aroused a lively discussion [49,131–138], since they conflicted with the view, established at the time, that the introduction of any bridge unit between a substituent and the reaction centre must lead to the weakening of the electronic interactions between them. Furthermore, the above phenomenon was initially observed

Table 7. Transmission coefficients in systems (I) with bridge heteroatoms (M).

No.	Reaction series	System (II)	M=—O—		M=—Se—		M=—S—		M=—NH—		M=—N(CH₃)—	
		ρ^0_{st}	ρ^0	π'	ρ^0	π'	ρ^0	π'	ρ^0	π'	ρ^0	π'
1	$ArNH_2 + 2,4,6\text{-}(NO_2)_3C_6H_2Cl \rightarrow 2,4,6\text{-}(NO_2)_3C_6H_2NHAr + HCl$; 25°, C_6H_6[34,128,129]	—1.56	—1.64[a]	1.05	—1.91[a]	1.23	—1.96	1.26	—2.15	1.38	—2.82	1.81
2	$ArNH_2 + 4\text{-}NO_2C_6H_4COCl \rightarrow 4\text{-}NO_2C_6H_4CONHAr + HCl$; 25°, C_6H_6[104,127]	—1.40	—1.48[a]	1.06	—	—	—1.88[a]	1.34	—	—	—	—
3	$ArNH_2 + C_6H_5COCl \rightarrow C_6H_5CONHAr + HCl$; 25°, C_6H_6[34]	—1.07	—	—	—	—	—1.70[b]	1.59	—1.92	1.79	—2.22[c]	2.07
4	$ArNH_2 + 4\text{-}NO_2C_6H_4SO_2Br \rightarrow 4\text{-}NO_2C_6H_4SO_2NHAr + HBr$; 25°, $C_6H_5NO_2$[41]	—1.44	—	—	—	—	—1.48	1.03	—1.67	1.16	—2.17	1.49
5	$ArNH_3^+ \rightleftarrows ArNH_2 + H^+$; 25°, H_2O[43,139]	0.89	1.12[d]	1.26	—	—	1.13	1.27	1.12	1.26	1.40	1.57
6	$ArNH_3^+ \rightleftarrows ArNH_2 + H^+$; 20°, 50% EtOH—$H_2O$[50,60,135]	0.98	0.92	0.94	—	—	—	—	—	—	—	—
7	$ArNH_3^+ \rightleftarrows ArNH_2 + H^+$; 25°, CH_3NO_2[140]	0.92[d]	0.79[d]	0.86	—	—	1.28[d]	1.39	1.17[d]	1.26	—	—
8	$ArCOCl + C_6H_5NH_2 \rightarrow ArCONHC_6H_5 + HCl$; 35°, C_6H_6[141,142]	0.32[e]	0.37	1.16	—	—	—	—	—	—	—	—
9	$HON_2ArN_2OH \rightleftarrows HON_2ArN_2O^- + H^+ \rightleftarrows {}^-ON_2ArN_2O^- + 2H^+$; 18°, H_2O[93]	1.73[f]	1.83[f]	1.06	—	—	2.12[f]	1.23	—	—	—	—
			π'_{av}	1.06±0.05		1.23		1.30±0.06		1.37±0.11		1.73±0.13

a, b, c, d Determined from two points for X = H and NO_2 (a), H and NH_2 (b), NH_2 and NO_2 (c), or NH_2 and $\overset{+}{N}H_3$ (d). [e] ρ^0_{st} was estimated from ρ^0 for benzene derivatives and the coefficient π'_{av} in Table 1. [f] The difference $pK_1 - pK_2$ is quoted.

only for certain properties (nucleophilic reactivity and basicity) of bridged amino-compounds (Table 6) and was not confirmed when other characteristics of the same substances (for example ultraviolet and Raman spectra) were considered[132,133]. However, it was found subsequently that an enhanced transmission efficiency is observed not only for the bridges listed in Table 6 but also for others (Table 4 and 5) when a large number of compounds (I) are investigated.

Table 7 (Nos. 1–7) presents data on the ability of amino-compounds to transmit electronic effects estimated from the values of ρ^0. The relations governing the variation of π'_{av} thus obtained agree well with the results in Table 6. As in the previous case, the maximum transmission of electronic influences is observed for diphenylamine derivatives. On passing from the biphenyl system to methyldiphenylamine, the sensitivity of the reaction centre to the influence of the substituent increases almost by a factor of two ($\pi'_{av} = 1.73 \pm 0.13$). The systems can be arranged in the following sequence (the bridges are indicated) in terms of their ability to transmit electronic effects: $-N(CH_3)- > -NH- > -S- > -Se- > -O-$. This is consistent (see below) with the ability of the above bridge groups to be involved in electron donor conjugation (p,π interaction).

2. The Nature and Mechanism of the Manifestation of PBE

Together with the increase of transmission efficiency of systems (I) with increase of the electron-donating capacity of the bridge heteroatom[143], mentioned above, the fact that the reactivity of these compounds correlates better with the σ^0,[43,140,143–145] characterising the influence of the substituted phenyl group $X-C_6H_4$, than with the Hammett constants σ is of great importance. On this basis, one may conclude that PBE is due to a combined transmission of the electronic influence, namely simultaneously via the inductive mechanism from one ring to the other and via the mechanism based on the conjugation of the bridge heteroatom with each benzene ring. This conjugation should depend on the inductive effect of the substituted phenyl group. The possibility of a change in the conjugation effects of various groups under the influence of the inductive effects of the substituents attached to them has been confirmed by numerous linear correlations between quantities characterising these effects (Zhdanov and Minkin[6], p. 375)[81,146–150].

Some information about the nature of the conjugation of the bridge heteroatom with the benzene rings in compounds (I) can be obtained by examining their geometrical structures. The molecules of these compounds are nonlinear, since the valence angles at the bridge heteroatom are much smaller than 180°[151–155] and, in consequence of their mutual repulsion, the *ortho*-hydrogen atoms in the benzene rings move apart, forming a dihedral angle φ. Their separation can be achieved in two ways[156,157]: (1) both rings are rotated relative to the C–M–C plane by the same angle $\varphi/2$; (2) one of the rings lies in this plane, while the other deviates from it by an angle φ. The problem of which situation actually obtains still remains open. In many instances[152,153,158–161] the first version appears to be preferred. Certain properties of symmetrical bridged bicyclic compounds calculated on this hypothesis agree fairly well with experimental data[159–161].

At the same time interest has been aroused by studies where it was concluded on the basis of an investigation of microwave[156], infrared, and Raman spectra[157] and dipole moments[156,162,163] that the two rings are equivalent in phenyl ether, diphenyl sulphide (and possibly diphenylamine[156], and their derivatives, i.e. that the second situation applies. It is natural to suppose that under these conditions the bridge heteroatoms can be preferentially conjugated first with one and then with the other

benzene ring and that this transition should be fairly rapid. Therefore methods where the duration of the measurement is longer than the lifetime of one of these states will yield averaged results [164], apparently indicating the equivalence of the conjugation of the bridge atom with the benzene rings. These methods include primarily electron and X-ray diffraction measurements [151]. On the other hand, in those cases where the duration of the measurement of the properties of the substance is shorter than the lifetime of the above molecular "species" the results must indicate their existence, which is consistent with certain spectroscopic data [156,157,165,166].

The satisfactory correlation of the reactivities of various bridged compounds with the σ^0 (Table 7) indicates the absence of a direct conjugation between the substituent and the reaction centre in the compounds. On the other hand, the conjugation in (I) between M and X and between M and Y is quite possible. Therefore the results in Table 7 agree best with the view that in systems (I) the bridge heteroatom is not conjugated simultaneously with both benzene rings.

Table 8.

No.	Bridge M in (I)	Reaction[a] of Compound Ar-NH_2	α	σ_R^{+} [7,34] p-CH_3—M—	$\alpha-\alpha_0$
1	—(biphenyl)	interaction with PC	0.47	—0.151	0.13
		" with BC	0.44	—	0.10
		" with PNBSB	0.62	—	0.28
		basicity	0.40	—	0.06
2	—CH_2—	interaction with PC	0.34	—0.200	0.21
		" with BC	0.24	—	0.11
		" with PNBSB	0.14	—	0.01
		basicity	0.35	—	0.22
3	—O—	interaction with PC	0.64	—0.604	0.51
		basicity	0.66	—	0.53
4	—S—	interaction with PC	0.81	—0.841	0.68
		" with BC	1.12	—	0.99
		" with PNBSB	0.80	—	0.67
		basicity	0.67	—	0.54
5	—NH—	interaction with PC	0.90	—1.09	0.77
		" with BC	1.28	—	1.15
		" with PNBSP	0.91	—	0.78
		basicity	0.66	—	0.53
6	—N (CH_3)—	interaction with PC	1.21	—1.26	1.08
		" with BC	1.49	—	1.36
		" with PNBSP	1.22	—	1.09
		basicity	0.85	—	0.72

[a]Abbreviations: PC = picryl chloride; BC = benzoyl chloride; PNBSB = p-nitrobenzenesulphonyl bromide.

Thus the manifestation of PBE in bridged amino-compounds is to a large extent due to the ability of the unshared electrons of the heteroatom to enter into electron-donor conjugation with the electronic system of the benzene rings. The constants σ_R^+ (Table 8), which reflect the ability of the p-CH_3-M group to enter into electron-donor conjugation with substituents R via the benzene ring, can be used as quantitative characteristics.

Fig. 1 shows that, for systems with single-unit bridges, there is a definite relation (with a correlation coefficient $r = 0.97$) between their transmission coefficient π'_{av} and σ_R^+. It is interesting to note that the point corresponding to the CH_2 group, where there are no unshared p electrons, also fits satisfactorily on the overall straight line. This most probably indicates that the above bridges interact similarly with the benzene rings in compounds (I). The σ, π conjugation of the methylene group can probably play a role, albeit to a much smaller extent, analogous to that of the p, π conjugation in systems with heteroatoms. The point corresponding to the sulphide bridge in Fig. 1 also fits on the overall straight line, despite the fact that the sulphur atom has vacant d orbitals, which may be involved in conjugation [167-173]. In this case it is probable that this property of the sulphur atom is hardly manifested or contributes in any way to σ_R^+ for the CH_3–S– group.

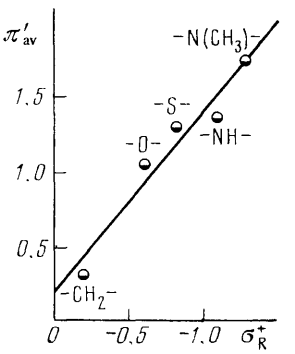


Figure 1. Variation of π'_{av} (Tables 2 and 7) for systems (I) with σ_R^+ (Table 8).

Taking into account the combined transmission of electronic influences in bridged systems, the observed value of ρ^0 for such systems should be linked with the transmission efficiency ρ_1^0 of the monocyclic system (for the same functional group and reaction conditions) by the relation (Palm [7], p. 231)

$$\rho^0 = \rho_1^0 (Z_p^* Z_M^* + \alpha Z_p^R). \qquad (2)$$

This equation reflects quantitatively the fact that the influence of the substituent in systems (I) with PBE is transmitted via both the inductive ($\rho_1^0 Z_p^* Z_M^*$) and conjugation ($\rho_1^0 \alpha Z_p^R$) mechanisms. The quantities Z_p^* and Z_M^* characterise the transmission of the inductive effect by the p-phenylene system and the M bridge, Z_p^R characterises the transmission of the conjugation effect by the p-phenylene system, and α is a measure of the change in the effect of the conjugation of the bridge group with the benzene rings due to the inductive effect of the substituent in the given reaction series.

The quantity ρ_1^0 can be obtained from the reactivities [34,35,44,174] of benzene derivatives by the equation

$$\lg k = \lg k_0 + \rho_1^0 \sigma^0 + \rho_R^+ \sigma_R^+ + \rho_R^- \sigma_R^- , \qquad (3)$$

where ρ_R^+ and ρ_R^- are constants characterising the sensitivity of the reaction series to the conjugation effect of the substituents of the type +R and –R, while $\sigma_R^+ = \sigma^+ - \sigma^0$ and $\sigma_R^- = \sigma^- - \sigma^0$.

The validity of Eqn. (2) was demonstrated using four reaction series for which the required values of ρ^0 (Table 7, Nos. 1 and 3–5) and ρ_1^0 (Table 1, Nos. 6, 8, 10, and 11) are available. Here it is important to stress that in the case of the corresponding monocyclic compounds (aniline derivatives) the effect of the electron-donor conjugation of the substituents ($|\rho_R^+| \gg 0$) [34,35,44] is shown to quite

an appreciable extent for all these series. The values of α calculated for single-unit bridge groups‡, subject to the condition that $Z_p^* = 0.11$, $Z_p^R = 0.43$, [175] and $Z_M^* = 0.40$ (Palm[7], p. 231), are listed in Table 8, which includes also the analogous data for the diphenylmethane system (calculated from the results of Table 2) and the non-bridged biphenyl system ($Z_M^* = 1.00$ according to the data in Table 1).

The α for single-unit bridges increase steadily with increasing capacity of the bridge groups for electron-donor conjugation. However, for a direct comparison of these quantities with the σ_R^+, it is necessary to subtract from them the constant α_0, which is due to the presence in the σ^0 of a resonance component equal to 0.145 σ^* (Palm[7], p. 236). The quantity $\alpha_0 = 0.145 Z_M^*/Z_p^R$ has a numerical value of 0.34 for systems (II) and 0.13 for systems (I) with single-unit bridges.

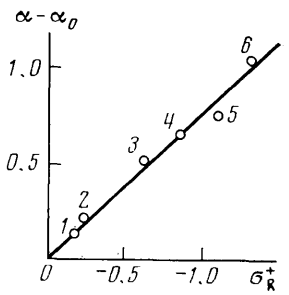


Figure 2. Variation of $\alpha - \alpha_0$ with σ_R^+ ($r = 0.99$) for the reactions of amines [Y = NH_3 in (I)] with picryl chloride. The symbols are numbered as in Table 8.

Comparison of the differences $\alpha - \alpha_0$ with the σ_R^+ (Table 8) shows that, for all the reaction series considered, there are linear relations (see the example in Fig. 2) which pass through the origin of coordinates, i.e. the relation given by the equation

$$\alpha - \alpha_0 = \beta\sigma_R^+. \qquad (4)$$

holds. It is noteworthy that the quantity $\alpha - \alpha_0$ for system (II) is positive (Table 8, No. 1) and the corresponding point in Fig. 2 fits satisfactorily on the common straight line for bridged systems. It is as yet difficult to explain this finding. However, the hypothesis that the inductive effect of the substituent influences the degree of conjugation (in the present instance the electron-donor conjugation) between the benzene rings does not lack justification.

‡It is assumed to a first approximation that the ability of the bridges to transmit electronic effects by the inductive mechanism is independent of their nature (Palm[7], p. 233). This conflicts with data on the correlation of the NMR spectra of fluoro-derivatives (Tables 5, 10, 11), for which the values of π'_I vary appreciably as a function of the nature of the bridge. The latter is probably due to the fact that, when the ^{19}F chemical shifts for such compounds are correlated, ρ_I is a more complex function than would appear from a formal examination of Eqn. (1).

Thus the results can serve as a quantitative confirmation of the above hypothesis that the influence of substituents on the functional activity of the reaction centre in type (I) amino-compounds is transmitted both by the inductive mechanism and by the mechanism based on electron-donor conjugation of the bridge heteroatom with each benzene ring. Here it is particularly significant that in the latter case the relative change in conjugation[176] under the influence of the substituent, defined by the product $\beta\sigma_R^+$ in Eqn. (4), and not its absolute magnitude, plays the principal role.

3. The Limits of the Manifestation of PBE

Since the capacity of the bridge group for electron-donor conjugation is not limitless, it follows that, as the electron-accepting properties of the substituents X in (I) become more pronounced, a situation may arise where this capacity has been completely exhausted. Subsequently the electronic influence on the reaction centre by the ring with the substituent must be transmitted preferentially via the inductive mechanism. In this case the plot of lg k against σ^0 will consist of two linear sections: one with a larger slope, where PBE is manifested, and one with a smaller slope, where there is no PBE. The abscissa (σ^0) of the break point may be designated by σ_{cr}^0 (Palm[7], p. 237).

The reactivities of 4-aminodiphenylamine with several electron-accepting substituents in the benzene ring without the reaction centre have been examined from this standpoint[177,178]. The findings agree qualitatively with the above considerations, but are somewhat complicated by the possibility of forming an intramolecular hydrogen bond between the imino-bridge and the *ortho*-substituent (nitro-group)[179-181].

More definite data were obtained in a study of the reactivities of triphenylamine derivatives with various substituents in the 4′- and 4″-positions[178,182,183]. The corresponding correlation graph, based on basicity data (Fig. 3*A*), agrees fully with the prediction. This suggests that in these systems the capacity of the bridge nitrogen for conjugation is already exhausted following the introduction of one nitro-group. On the other hand, in the reactions of these amines with *p*-nitrobenzenesulphonyl bromide (PNBSB) this situation is attained following the introduction of two nitro-groups (Fig. 3*B*), while the reaction with picryl chloride could not be achieved in the experimental $\Sigma\sigma^0$ range (Fig. 3*C*).

Comparison of the ρ^0 for different sections of the correlation graph in Fig. 3 with the analogous values for aminobiphenyl derivatives [system (II)] in the same reaction series makes it possible to estimate the ability of the bridge group to transmit electronic effects in its various states. In those cases where the capacity of the bridge nitrogen atom for conjugation has not been fully exhausted (the left-hand branches *A* and *B* and straight line *C*), PBE is clearly manifested (the π' are respectively 1.17, 1.29 and 1.24)[34,41,182]. After σ_{cr}^0 has been reached (the right-hand branch *A*), the transmission coefficient of the nitrogen atom ($\pi' = 0.21$) [178] is much smaller than for the methylene unit in system (I) (Table 2). Furthermore, it is smaller by a factor of two than the coefficient defining the capacity of this unit for transmission of electronic effects by the inductive mechanism alone (0.388). The extremely low transmission coefficient obtained for the electron-deficient nitrogen atom agrees satisfactorily

with π' for the positively charged nitrogen atom in *N*-protonated derivatives of *N*-arylglycines (0.22) [183,184] and the nitrogen atom in the amide group (0.23) [185].

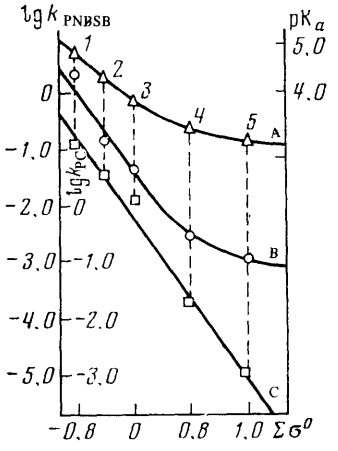


Figure 3. Variation with $\Sigma\sigma^0$ of pK_a (A) for triphenylamine derivatives [4′-X-C_6H_4-N(Ar)-C_6H_4-NH_2-4] in 45% aqueous dioxan [162] and of lg *k* for the reactions of these amines with nitrobenzenesulphonyl bromide (B) in nitrobenzene and with picryl chloride (C) in benzene [166] at 25°C; X and Ar in the formula: 1) 4′-NH_2, 4″-NH_2. .C_6H_4; 2) 4′-NH_2, C_6H_5; 3) H, C_6H_5; 4) H, 4″-$NO_2C_6H_4$; 5) 4′-NO_2, 4″-$NO_2C_6H_4$.

All these findings show that PBE can be manifested only in those cases where the reaction series investigated (for benzene derivatives as an example) is sufficiently sensitive to electron-donor conjugation [ρ_R^+ in Eqn. (3) differs significantly from zero] and the bridge group M in compounds (I) has unshared electrons capable of being involved in such conjugation.

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On the basis of the principles formulated above, it is interesting to examine data describing the ability of systems (I) with bridge heteroatoms to transmit electronic effects, which have been obtained from other reaction series (Y ≠ NH_2). Since the reaction of benzoyl chloride derivatives with aniline is fairly sensitive to the electron-donor conjugation of substituents [186], the manifestation of PBE in the phenyl ether system for Series No. 8 (Table 7) becomes quite understandable. For the same reason (high sensitivity to the above conjugation [137], an enhanced transmission efficiency of systems (I) with M = –O– and –S– is observed in Series No. 9 (Table 7).

It is interesting that, in a study of the transmission efficiencies of systems (I) on the basis of acid dissociation data (Y = OH), Frankovskii and coworkers [49,50,135–137] concluded that the bridge heteroatoms have an insulating influence. At the same time their results (Table 9) show that in this case the transmission efficiency increases in the sequence (the bridges M are indicated) –O– < –S– < –NH–, while in the case where M = –NH– it virtually coincides with that of system (II). The parallel variation of the π' in Table 9 and the σ_R^+ for CH_3–M groups (Table 8) suggests that in this case the capacity of the bridge atom for electron-donor conjugation plays a significant role. Since the acid dissociation of phenols is almost insensitive to such conjugation ($\rho_R^+ = 0$) [44], it follows that the higher values of π'_{av} in Table 9 compared with the coefficient giving the transmission efficiency for a single-atom bridge solely by the inductive effect (0.388) is due to the conjugation of the bridge heteroatom with the benzene ring containing this substituent and not with the ring in which the reaction centre is located. This constitutes direct confirmation that the manifestation of PBE requires that the bridge heteroatomic group should enter into electron-donor conjugation with each benzene ring.

Table 9. Transmission coefficients in systems (I) (Y = OH) with bridge heteroatoms.

No.	Reaction series	System (II)	M=—O—		M=—S—		M=—NH—	
		ρ_{st}	ρ	π'	ρ	π'	ρ	π'
1	ArOH ⇄ ArO^- + H^+; 20°, 60% EtOH–H_2O [49,50,135,137]	0.81	0.39	0.48	0.55 0.57[a]	0.68 0.70	0.77	0.95
2	ArOH ⇄ ArO^- + H^+; 20°, 60% dioxan-water [135–137]	0.76	0.29	0.38	0.57 0.76[a]	0.75 1.00	0.73	0.96
3	ArOH ⇄ ArO^- + H^+; 20°, 60% acetone-water [50]	0.99	0.44	0.44	0.59 0.72[a]	0.60 0.73	0.88	0.89
			π'_{av}	0.43±0.03	0.68±0.04 0.81±0.10[a]		0.93±0.02	

[a] The X-(2′-Cl)-C_6H_3-S-C_6H_4-Y-4 system is considered.

Comparison of the chemical shifts (Table 10) in the NMR spectra of compounds of type (I) shows that, as expected, there is no full correspondence between the series being compared. For fluorobenzene derivatives, where the chemical shift depends significantly on the effect of the electron-donor conjugation of the substituents (Zhdanov and Minkin [6], p. 375), the introduction of bridge heteroatoms between the benzene rings (Table 10, Nos. 1–3) leads to an increased influence of the substituent on the given property, i.e. PBE is clearly manifested in this instance. On the other hand, measurements of the chemical shifts due to the proton in the hydroxy-group have shown that, although the ability of bridge groups to transmit electronic effects does increase on passing from oxygen to nitrogen, it does not exceed that of system (II). As for the acid dissociation of the above compounds (Table 9), the absence of PBE in this case is caused by the insensitivity of the proton chemical shifts in the series of phenol derivatives to the electron-donor conjugation of substituents [78].

An enhanced transmission coefficient of the heteroatom ($\pi' > 1.0$) has been observed in a study of NMR spectra also in other series where the bridge heteroatom was incorporated between two π-electron systems (for example a benzene ring and a vinyl group) [171–173,188]. The transmission coefficient of the system with M = –S– then proved to be greater than for M = –O–.

The full analogy between the results obtained in measurements of the reactivities of amino-compounds

(Table 7) and the ^{19}F chemical shifts (Table 10) for compounds of type (I) with bridge heteroatoms suggests that Eqns. (2) and (4) are applicable to the latter case. Indeed, Fig. 4 shows that the relation between the α calculated from the data in Table 10 and the σ_R^+ (Table 8) is described by a straight line passing through the coordinate origin, in accordance with Eqn. (4). The point for diphenylmethane fits on the same line, as in Fig. 2. However, the point for system (II) deviates appreciably from the general line, which is probably due to the characteristic features of the transmission of electronic influences in the series of fluoro-derivatives (see below).

Table 10. Transmission coefficients estimated from NMR spectra in systems (I) with bridge heteroatoms.

No.	Bridge M in (I)	Y=^{19}F[86,103]			Y=^{19}F[87]	Y=OH[50,80]
		π_I'	π_R'	n[a]	π'	π'
1	—O—	1.00±0.01	1.08±0.01	9	1.10[b]	0.52[c]
2	—S—	1.21±0.01	1.42±0.01	9	1.51[b]	—
3	—NH—	1.50	1.84	1	—	0.76[c]
4	—$\bar{C}$Ph—	3.34	2.86	1	—	—
5	—N=$\bar{C}$—	2.74	1.80	1	—	—

[a]The number of solvents in which bridged compounds of types (I) and (II) were investigated. [b]Estimated by a direct comparison of the values of $\Delta\delta$. [c]The chemical shifts of the hydroxyl proton were measured and compared.

The highest transmission coefficient in the series of fluoro-derivatives has been observed for the $-\bar{C}Ph-$ bridge (Table 10, No. 4) bearing an integral negative charge, which maximises its capacity for electron-donor conjugation. An enhanced transmission coefficient has also been observed for the $-N=\bar{C}-$ bridge (No. 5) whose capacity for conjugation should be fairly high.

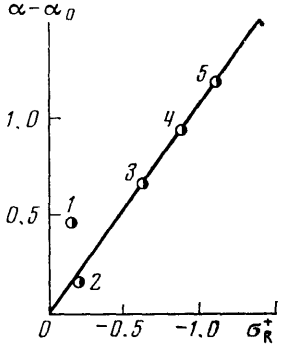


Figure 4. Variation of $\alpha - \alpha_0$ with σ_R^+ ($r = 0.99$) for systems (I) with M = $-CH_2-$ (*2*), $-O-$ (*3*), $-S-$ (*4*), and $-NH-$ (*5*) and for system (π) (*1*) on the basis of NMR (Y = ^{19}F) [86,103].

Analysis of the corresponding infrared spectroscopic data for a series of benzoic acid derivatives (the C=O stretching vibration frequencies) indicates their high sensitivity to electron-donor conjugation by the substituents ($\rho_R^+ \gg 0$). This is precisely why PBE was observed in studies by this method of compounds of type (I) with Y = $COOCH_3$ and M = $-O-$. [145,189]

PBE was also observed in a study of the stretching vibration frequencies of N – H in compounds (I) with Y = NH_2 in the presence of bridges such as $-O-$, $-S-$, $-NH-$, and $-N(CH_3)-$. [43] This is fully consistent with the above considerations, since the frequencies for aniline derivatives [190] depend significantly on the capacity of the substituents for electron-donor conjugation.

Thus data derived from NMR spectra (Table 10) and infrared spectra of compounds of type (I) fully confirm the conclusions reached about the mechanisms and characteristics of the manifestation of PBE obtained in studies on the reactivities of the corresponding compounds (Tables 7 and 9).

V. SYSTEMS WITH SINGLE-UNIT BRIDGE GROUPS CAPABLE OF ELECTRON-ACCEPTOR CONJUGATION

The data examined above concerning the manifestation of PBE refer mainly to systems (I) where the bridge consists of heteroatoms capable of electron-donor conjugation. It is reasonable to suppose that, in those cases where the reaction series is characterised by a high sensitivity to the electron-accepting effect of the substituents ($|\rho_R^-| \gg 0$), PBE can also be manifested in systems (I) with bridge groups capable of electron-acceptor conjugation.

For reactions involving substituted anilines, ρ_R^- in Eqn. (3) is fairly high. This is in fact why studies on the nucleophilic reactivity of 4'-derivatives of 4-aminobenzophenone [21,191] yielded $\pi'_{AV} = 0.91$ (for reactions with *p*-nitrobenzoyl chloride and picryl chloride). This shows that system (I) with M = $-CO-$ hardly differs from system (II) in its ability to transmit electronic effects, i.e. an enhanced transmission efficiency was observed for the first time in bycyclic systems with bridge groups capable of electron-acceptor conjugation.

Subsequently enhanced transmission efficiencies of systems (I) with the above bridge groups were observed in studies of the acid dissociation of the corresponding hydroxy-compounds (Tables 3 and 4) and the NMR spectra of fluoro-derivatives (Table 5). Here it is important to emphasise that in the cases examined PBE is shown only for fairly powerful electron-accepting bridge groups and varies in the sequence $-NR=CH- > -CH=NR- > -N=N-$, i.e. in the same sequence as the electron-accepting capacity of these bridges. For groups with weaker electron-accepting capacities, such as $-CH=N-$, $-N=CH-$, $-C\equiv C-$, and $-CH=CH-$ (Tables 3–5), the coefficients π' are appreciably less than unity.

These bridges do not show high transmission efficiencies for systems (I) (Tables 3–5), although all the reaction series examined (with the exception of Nos. 7 and 8 in Table 3) are sensitive to electron-acceptor conjugation [when data for benzene derivatives are interpreted in terms of Eqn. (3), the ρ_R^- are non-zero]. This shows that PBE is observed only after the attainment of a specific capacity of the bridge group for electron-acceptor conjugation and when the reaction centre is highly sensitive to such conjugation. This is confirmed also by measurements of the transmission coefficients of systems (I) with M = $-SO_2-$. Whereas according to the dissociation data for 4-hydroxy-derivatives $\pi' = 1.24$ in the

diphenyl sulphone system[50] (i.e. PBE is clearly manifested), the study of the nucleophilic reactivities of the corresponding 4-amino-derivatives with respect to picryl chloride in nitrobenzene showed that $\pi' = 0.68$ (PBE not observed)[192].

Since the NMR spectra of fluorobenzene derivatives are fairly sensitive to both electron-donor and electron-acceptor conjugation (Zhdanov and Minkin[6], p. 375), it is quite reasonable that, in NMR studies of compounds of type (I) (Y = ^{19}F), PBE is observed for both electron-donating (Table 10) and some electron-accepting (Table 5) bridge groups. As already stated, in the latter case, PBE is not observed in all cases but only for the most electron-accepting bridges§. This hypothesis is confirmed particularly clearly by the data in Table 11, where the transmission coefficients for bicyclic systems with single-unit bridges increase steadily as the electron-accepting properties of the bridge group and its capacity for electron-acceptor conjugation become more marked, reaching a maximum value ($\pi'_I = 13.9$) for the powerful acceptor $-\overset{+}{C}(CF_3)-$ (No. 11).

Table 11. Transmission coefficients estimated with the aid of NMR in systems (I) with single-unit electron-accepting bridges.

No.	Bridge M in (I)	Y=^{19}F[86,103]		Y=^{19}F[87]
		π'_I	π'_R	π'
1	$-\overset{CH_2}{\overset{\parallel}{C}}-$	—	—	0.48[a]
2	$-\overset{O}{\overset{\parallel}{C}}-$	0.73	0.59	0.76[a]
3	$-\overset{NH}{\overset{\parallel}{C}}-$	0.82	0.63	—
4	$-\overset{O\cdot BF_3}{\overset{\parallel}{C}}-$	1.82	1.35	—
5	$-\overset{O\cdot BCl_3}{\overset{\parallel}{C}}-$	2.23	1.56	2.44[a]
6	$-\overset{O\cdot BBr_3}{\overset{\parallel}{C}}-$	2.24	1.61	—
7	$-\overset{+}{C}(OH)-$	2.26	1.69	2.72[a]
8	$-\overset{+}{C}Ph-$	3.14	2.40	—
9	$-\overset{+}{C}(CH_3)-$	5.80	4.86	—
10	$-\overset{+}{C}H-$	7.07	5.29	—
11	$-\overset{+}{C}(CF_3)-$	13.9	10.4	—

[a]Estimated by a direct comparison of the values of $\Delta\delta$.

Unfortunately, owing to the lack of $\sigma_{\bar{R}}$ constants, characterising the capacity of the CH_3–M– groups for electron-acceptor conjugation, it was not possible to interpret the data considered in the present section in terms of equations analogous to Eqns. (2) and (4).

It is interesting that the coefficients π'_R calculated from the corresponding ρ_R constants increase in parallel with increase of the π'_I (Tables 5, 10, and 11). The reasons for the observed variation of these constants as the bridge M in (I) is varied are not yet altogether clear. Nevertheless, it is noteworthy that the very appearance of the constants ρ_R, which usually characterise the interaction between the substituent and the functional centre via the conjugation mechanism, can hardly be caused here by this interaction. The point is that the ρ_R are not zero even in series such as p-X–C_6H_4–CH_2–^{19}F, p-X–CH_2–C_6H_4–^{19}F, and p'-X–C_6H_4–CH_2–C_6H_4–^{19}F-p, [103] where such conjugation should not occur.

The above data permit the conclusion that in bridged bicyclic systems of type (I) the electronic interaction between the substituent and the reaction centre can be not only weaker than in the non-bridged biphenyl system (II) but in some cases can also be several times stronger. This enhancement of the interaction, i.e. the positive bridge effect, is manifested distinctly only when the following conditions are observed:

1. The reaction series investigated (Ar–Y) is fairly sensitive for benzene derivatives to electron donor (or electron-acceptor) conjugation, i.e. the constant $\rho_{\dot{R}}$ (or $\rho_{\bar{R}}$) in Eqn. (3) is appreciably different from zero.
2. The bridge group can be involved in the above conjugation, i.e. $\sigma_{\dot{R}}$ (or $\sigma_{\bar{R}}$) for the CH_3–M– group is much smaller (or greater) than zero.
3. The bridge group is conjugated with each benzene ring to an extent which varies as a result of the inductive effect of the substituted ring.

§The deviation of the point for system (II) in Fig. 4 (No. 1) is probably caused by the enhanced transmission efficiency due to the capacity of the benzene ring for electron-acceptor conjugation.

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