

We will now attempt to determine how quantitative these correlations can be made. If the measured activity coefficients of the models chosen represent accurately the true behavior of the indicators, we should be able to calculate the other acidity functions from just one of them and the activity coefficient data. We have chosen to calculate H_O and H_R' from H_- according to the equations

$$H_O = H_- + \log (f_{BH^+} f_{A^-}) - \log f_B - \log f_{HA} \quad (19)$$

$$H_R' = H_- + \log (f_{R^+} f_{A^-}) - \log f_{ROH} - \log f_{HA} \quad (20)$$

For the H_O function calculation, f_{BH^+} was taken to be that for *p*-nitroaniline and f_B to be that for 2,6-dichloro-4-nitroaniline. For the H_R' calculation f_{R^+} is that for tri-(*p*-methoxyphenyl)-carbinol and f_{ROH} for triphenylcarbinol. The latter activity coefficient was estimated at 60 and 70% acid concentration by assuming that its variation is parallel to the others in Fig. 2 in that concentration range. To represent H_- activity coefficients, f_{A^-} was taken to be that for pentacyanopropene, and f_{HA} to be that for *p*-chloro-N-tricyanovinylaniline.

The results of the calculation of H_O and H_R' from H_- are shown in Table III. The agreement with the experimental H_O is good and reproduces this function fairly well over the entire acid concentration range studied. The agreement with H_R' is also good, the calculated values being about 0.4 unit higher over most of the concentration range.

Perhaps most closely related to the hydrogen ion activity itself would be the quantity

$$\log (a_{H^+}/f_{TEA^+})$$

which is given by

$$\log a_{H^+} - \log f_{TEA^+} = -H_- - \log f_{A^-} + \log f_{HA} \quad (21)$$

This was also calculated under the above assumptions and is shown in Table III.

Acknowledgment.—The author is greatly indebted to the University Research Council, Utah State University, and to the National Science Foundation (Grant GP-198) for financial support. He is also grateful to Mr. Richard E. Wuthrich for assistance in carrying out the experimental work.

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Interaction of Perpendicular π -Electron Systems

By H. H. JAFFÉ¹ AND O. CHALVET

RECEIVED AUGUST 1, 1962

The spectra of a series of phenyl-substituted naphthalenes⁴ are interpreted in terms of a resonance interaction of the substantially perpendicular π -electron systems of the naphthalene skeleton and the phenyl groups.

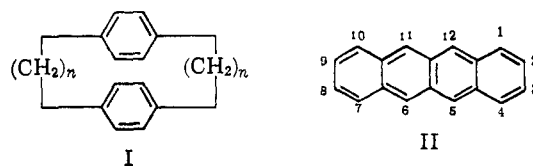
It has long been assumed in the discussion of the chemistry, and particularly of the spectroscopy of conjugated organic systems, particularly hydrocarbons, that two π -electron systems having perpendicular nodal planes do not interact at all with one another, with the possible exception of some minor inductive effect. Thus, for instance, in the calculation of the angle of twist in biphenyl,² the spectrum of the completely twisted model is assumed to be identical to twice that of an isolated benzene; the pure inductive effect of one phenyl on the spectrum of the other is ignored since pure inductive effects are well known to have little importance in the spectra of alternate systems. Any careful test of these assumptions is extremely difficult, because, in general, the two perpendicular π -electron systems are of approximately equal size, and hence their spectra are usually well confounded. Also, it is generally difficult to obtain systems where the nodal planes must really be perpendicular to one another.

The problem seems to have received only very little prior theoretical consideration. The only work³ which appears to consider seriously the effect of one π -electron system on another ascribes all interaction to electron repulsion integrals. Although these undoubtedly make some contribution, the method has not been applied to any system in which experimental verification is available.

A particularly favorable system is that of the various phenyl-substituted naphthalenes, which has recently been carefully investigated.⁴ In this system the naphthalene skeleton has an electronic spectrum in the visible region (400–470 $m\mu$) with a well developed vi-

brational structure, quite far separated from the absorption of the phenyl substituents. In addition, substitution of two phenyl groups in positions *peri* to one another leads to such severe steric strain that any orientation of the phenyl rings other than perpendicular (or virtually so) to the naphthalene skeleton is unthinkable. The presence of two phenyl groups *peri* to one another provides another highly interesting feature: Two such rings will lie substantially parallel to one another, and hence will be subject to similar types of interaction as the *p*-cyclophanes (I).⁵ These interactions are well known to leave the ground state substantially unaffected, but to stabilize considerably the first excited state.⁶

The results in the phenyl naphthalenes are particularly striking, since the longest wave length absorption band, the ${}^1L_a \leftarrow {}^1A$ band in Platt notation, even on substitution of naphthalene (II) by several phenyl groups, retains its characteristic vibrational structure, hence is readily recognized as corresponding to the same electronic excitation, and thus permits the recognition of the effect of phenyl substitution on the naphthalene π -electron system. Substitution of a single phenyl group in either the 1- or 5-position produces a significant batho-



chromic shift, as shown in Table I. This shift might well be interpreted as due to a resonance interaction of the phenyl group with the naphthalene, assuming that

(5) D. J. Cram, *et al.*, *J. Am. Chem. Soc.*, **73**, 569 (1951); **76**, 6132 (1954); **80**, 3115 (1958); **81**, 5963 (1959).

(6) L. L. Ingraham, *J. Chem. Phys.*, **18**, 988 (1950); *cf.* also H. H. Jaffé and M. Orchin, "Theory and Applications of Electronic Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, Ch. 15.

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(2) H. Suzuki, *Bull. Chem. Soc. Japan*, **32**, 1340, 1350 (1959).

(3) H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc. (London)*, **A68**, 601 (1955); *J. Chem. Soc.*, 2552 (1955).

(4) R. G. Douris, *Ann. Chim.*, **4**, 479 (1959).

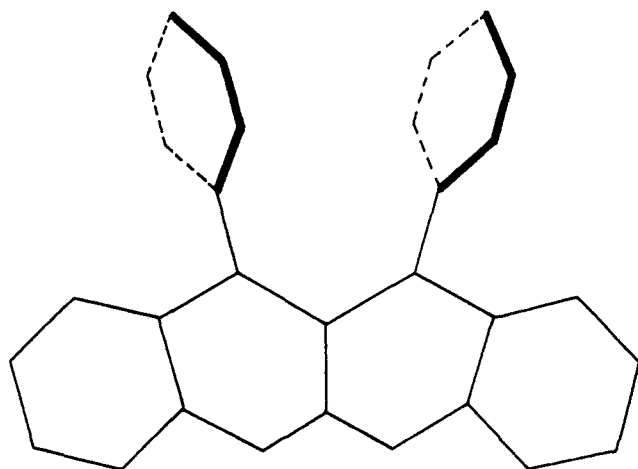


Fig. 1.—Diphenylnaphthacene.

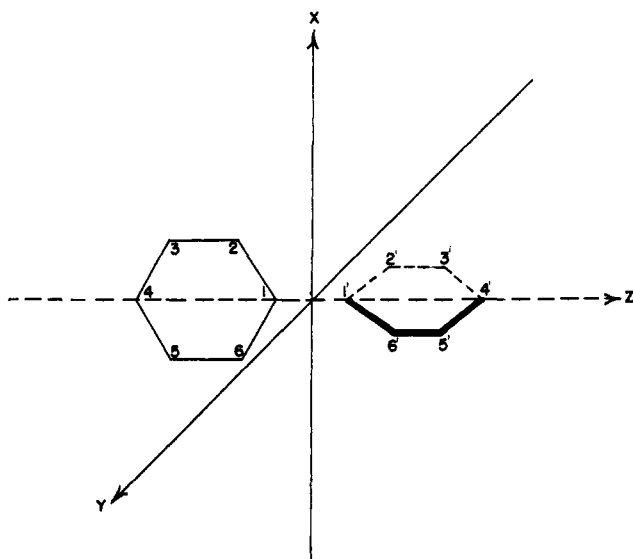


Fig. 2.—Perpendicular biphenyl.

the two groups, although not nearly in one plane, are not completely perpendicular to one another. This interpretation is rendered quite likely since the shift caused by a 1-phenyl group, which undoubtedly is less out of plane because of smaller steric hindrance, is considerably greater than the shift caused by a 5-phenyl group. Since apparently the phenyl groups produce only a minor perturbation, it is not surprising that phenyl groups in non-adjacent positions produce substantially additive effects (Table I).

TABLE I
SHIFTS IN THE LONGEST WAVE LENGTH BAND (2103 CM.⁻¹) OF
THE SPECTRUM OF NAPHTHACENE (IN CM.⁻¹)

	ν^a	$\Delta\nu$
Naphthacene	21030	...
5-Phenyl	20660	-370
5,12-Diphenyl	20280	-750
5,6-Diphenyl	20140	-890
5,6,11-Triphenyl	19840	-1190
5,6,11,12-Tetraphenyl	18900	-2130
1,6,11-Triphenyl	19980	-1050
1,4,6,11-Tetraphenyl	19680	-1350
5,11-Diphenyl	20280	-750

^a These values apply to the longest wave length vibrational component of the band; however, the vibrational structure remains unchanged, and the differences are virtually the same for all components.

The effect of introducing two phenyl groups in neighboring (*peri*) positions is, however, considerably

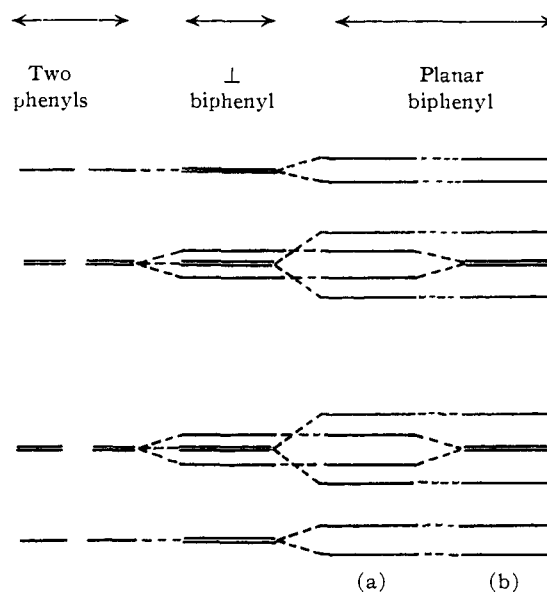


Fig. 3.—Energy level and correlation diagram for perpendicular biphenyl (including non-neighboring interactions) with the separate phenyls, and planar biphenyl with (a) and without (b) the same non-neighbor interactions.

greater than the sum of the effects of the separate substitutions in the corresponding positions, and this fact indicates that the above simple interpretation is inadequate. Since two *peri*-phenyl groups must tremendously interfere with each other, the simple theory would have predicted that the non-planarity of the system is increased, and consequently the resonance interaction between phenyl and naphthacene is decreased and the bathochromic effect is reduced.

Assuming for the moment that the naphthacene skeleton is not distorted by phenyl substitution, and that bond angles retain their normal values, the distance between two *peri*-phenyl groups is of the order of 2.40 Å., an extremely close approach for non-interacting systems. Undoubtedly, some distortion of the naphthacene skeleton and, even more important, of the naphthacene-phenyl bond angles will occur, but will still leave the phenyl groups at very close distances. It seems extremely unlikely that these distortions can lead to the bathochromic shifts observed, since ring distortions seem to produce hypsochromic shifts. The very low phenyl-phenyl distance seems to require complete perpendicularity of the phenyls to the naphthacene, even though the distortions may not leave the phenyls perfectly parallel, as indicated in Fig. 1.

In the light of these geometric requirements, the excess bathochromic effect (over the additive effect of two phenyls) seems to be most readily interpreted in terms of an interaction between the phenyl groups of the same type as found in the cyclophanes.⁶ In these compounds this interaction leads immediately and unequivocally to the bathochromic effects noted, since the excited state affected by the interaction is a state of the π -electron system in which the interaction occurs. In the case of the diphenylnaphthacene, however, the interaction of the phenyl groups affects the excited state of the π -electron system of the *phenyl groups*. Hence the bathochromic effect on the *naphthacene* spectrum is unexpected, since, as discussed above, no interaction between perpendicular π -electron systems is anticipated. Thus the experimental data strongly suggest that perpendicular π -electron systems do interact, and the nature of this interaction must now be examined.

It is perhaps easiest to discuss this interaction for the simple case of a perpendicular biphenyl. Qualitatively,

the interaction is easiest seen by examining the symmetry properties of the molecular orbitals of each phenyl group. In the π -electron approximation, six MO's need to be considered. For each of these, the plane of the group is a nodal plane. A second plane of symmetry of the phenyl group is a plane through a pair of *para* carbon atoms and perpendicular to the group plane. With respect to this plane, four MO's are symmetric, two antisymmetric. Of the two antisymmetric MO's, one belongs to the degenerate pair of highest occupied orbitals, one to the degenerate pair of lowest unoccupied orbitals. In the perpendicular biphenyl molecule, Fig. 2, the nodal plane of all MO's of phenyl group A is the xz -plane, and for phenyl group B the yz plane. But the other nodal plane for the two antisymmetric MO's of group A is the yz -plane, for group B the xz -plane. Thus these orbitals have the same planes of symmetry, and hence can undergo interaction. Such interaction may be important provided the interaction integrals are not zero or vanishingly small.

Perhaps a more fundamental, but less readily visualized way of seeing the interaction, and, at the same time, of considering the magnitude of the interaction term, depends on setting up the secular determinant for the 12-center 12-electron system of biphenyl. In the normal manner of doing so, resonance integrals between any non-neighboring atoms are neglected. Thus, the only resonance integral connecting the minors corresponding to the two phenyl groups is $\beta_{11'}$. This integral, however, vanishes identically for perpendicular biphenyl because the π -orbitals of atoms 1 and 1' are perpendicular to each other, *i.e.*, they have perpendicular nodal planes. Consequently the determinant factors into two identical parts, giving the energy levels of benzene, which are shown in the left column of Fig. 3.

If, however, the β_{rs} for non-neighboring r and s are not neglected, it is readily found that the β between atoms 2, 3, 5, 6 and their primed counterparts do not vanish identically. Obviously, there are also a number of non-vanishing such β within each ring; these are, however, of little interest here since they affect the separate phenyls and the whole molecule equally. Among the non-vanishing inter-ring β , $\beta_{22'}$, $\beta_{26'}$, $\beta_{62'}$ and $\beta_{66'}$ will have the largest, and probably significant values.⁷ These terms prevent the factoring of the matrix. It can readily be shown by perturbation theory that the energy level diagram of the resulting biphenyl must have the form shown in Fig. 3. It is immediately obvious that this interaction leads to a bathochromic shift of the long wave length absorption. It is instructive to complete the correlation diagram to planar biphenyl. At the extreme right of Fig. 3, a conventional energy level diagram of planar biphenyl is given. The non-neighbor interactions will modify this diagram as shown. It is particularly interesting to note that it is just the pairs of energy levels which are degenerate in planar biphenyl (conventional) which are split by the interaction discussed in the perpendicular case.

The interaction in the phenylnaphthalenes here postulated is of the same type. The orbitals of the phenyl group having the nodal planes described above (the antisymmetrical MO's) interact with naphthalene orbitals having nodal planes perpendicular to the naphthalene plane and through the atom at which the phenyl group is attached, and, to a lesser extent, with any orbital which is not symmetrical with respect to such a plane. Orbitals with such nodal planes are

(7) A related use of non-neighboring β 's is suggested by H. Preuss, *Tetrahedron*, in press, although not used in the treatment of spectroscopic data. Preuss has, however, neglected the particular β 's of importance in the present discussion.

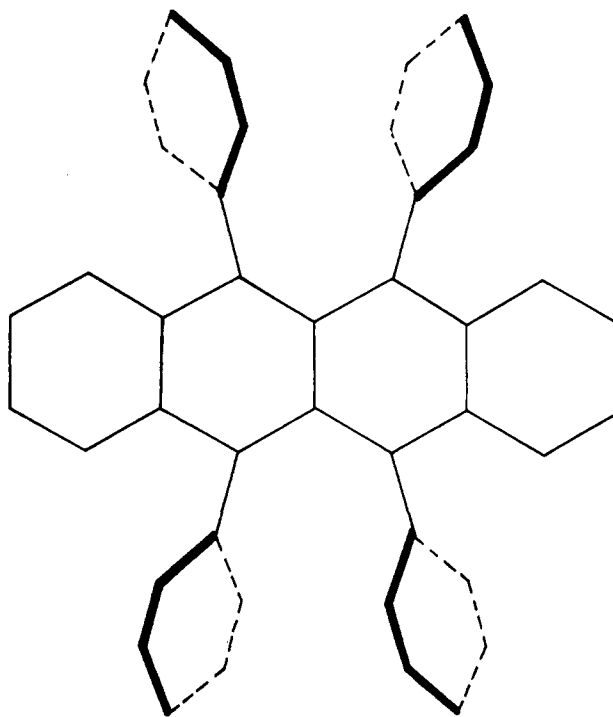


Fig. 4.—Rubrene.

available in naphthalene, and most other polycyclic hydrocarbons.⁸ Thus a mechanism for interaction of the perpendicular π -electron systems is available.

Next, it must be shown that the interaction of two parallel phenyl π -electron systems will actually lead to a bathochromic effect in the naphthalene system. In order to avoid too extensive computation, a highly simplified model was chosen. In this model the naphthalene is replaced by naphthalene, *i.e.*, the outer two rings are neglected. Since only the "antisymmetric" orbitals of the phenyl groups are of interest, these groups were replaced by vinyl groups, which have substantially the same symmetry properties, and the small naphthalene-phenyl interaction was taken into account by using a small naphthalene-vinyl resonance integral (0.1β). Finally, the phenyl-phenyl interactions were introduced by allowing the resonance integrals β_r between corresponding atoms of neighboring vinyl groups to assume various small but non-zero values. The data obtained, shown in Table II, indicate that the

TABLE II
SHIFTS CALCULATED IN "VINYLNAPHTHALENES" AS A FUNCTION OF INTERVINYL β_r (IN β)

Compound	β_r^a	ν	$\Delta\nu^b$ vinyl	$\Delta\nu^c$ inter- vinyl
Naphthalene	...	1.2361
1-Vinyl-	...	1.2325	0.0036	...
1,4-Divinyl-	...	1.2289	.0072	...
1,5-Divinyl-	...	1.2289	.0072	...
1,8-Divinyl-	0.0	1.2289	.0072	...
	.1	1.2283	...	0.0006
	.3	1.21770112
	.5	0.98642425
1,4,5,8-Tetravinyl-	.0	1.2254	0.0107	...
	.1	1.2248	...	0.0006
	.3	1.21440110
	.5	0.98622392
	.7	0.59556299

^a The β_r for interaction of the two vinyl groups. ^b Effect of vinyl-naphthalene interaction. ^c Effect of vinyl-vinyl interaction.

(8) C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants," Vol. II.

interaction of the vinyl groups actually leads to a bathochromic shift. For very small β_r this effect appears to be very small, but it is seen (Table II) to increase rapidly with β_r , at a rate which itself increases rapidly with β_r in the region most likely to be of interest (0.1–0.5). The extreme crudeness of the model and the complete uncertainty as to the values to be assigned to the various resonance integrals makes any *numerical* values meaningless, but the direction of the shift may be taken as established.

Table I also lists data for 5,6,11,12-tetraphenylnaphthacene (rubrene) which show an additional increment over twice that observed for the 5,6-diphenyl compound. This additional increment does not arise in the calculations with the model used, and probably would not arise in a more realistic model. It seems very probable that this last increment arises out of steric relations. The distortion of the naphthacene suggested in Fig. 1 cannot, because of symmetry, persist in rubrene. The introduction of the two additional phenyls should then push the first two phenyls closer together (see Fig. 4), thus increasing the interphenyl interaction, and leading to the observed additional increment.

The same work which reports the phenylnaphthacenes also reports a corresponding series of chloronaphthacenes.⁴ Qualitatively, the effects are similar, as seen in Table III, although quantitatively the interaction terms between adjacent chlorines are much greater than in the phenyl series. The interpretation is probably quite similar, although, of course, the chlorine atoms undergo direct resonance interaction with the naphthacene π -electron system. The final increment, due to the steric distortion in the tetrachloro compound is also observed. It seems quite probable that chlorine d-orbitals are involved in the interaction between neighboring chlorines.

TABLE III
SHIFTS IN CHLORO- AND CHLOROPHENYLNAPHTHACENES
(IN CM. ⁻¹)

	ν^a	$\Delta\nu$
Naphthacene	21030	
3-Chloro	20470	-560
5,12-Dichloro	19980	-1050
5,6,11-Trichloro	19120	-1910
6-Chloro-5,12-diphenyl	19530	-1500
6-Chloro-5,11-diphenyl	19550	-1480
10-Chloro-5,6-diphenyl	19680	-1350
6,11-Dichloro-5,12-diphenyl	18770	-2260
6,12-Dichloro-5,11-diphenyl	18760	-2250
5,6-Dichloro-11,12-diphenyl	18450	-2580

^a These values apply to the longest wave length vibrational component of the band; however, the vibrational structure remains unchanged, and the differences are virtually the same for all components.

In addition to the two series discussed, a number of phenylchloronaphthacenes have been examined.⁴ Again, the same effects are observed, and are most likely produced by the same mechanism. The most striking observation is the apparent interaction between chlorine atoms and neighboring phenyl groups. This interaction is again readily explained since the p- and d-orbitals of chlorine having π -character with respect to the naphthacene system can interact with the phenyl orbit-

als which are postulated to cause the bathochromic effect, and, in addition, other chlorine orbitals have appropriate symmetry to interact with these, and with other phenyl orbitals.

Finally, the few observations reported on the phenyl-anthracenes follow the same pattern.⁴

Conclusions

The fact that two phenyl groups substituted in *peri* positions in naphthacene produce a bathochromic effect on the naphthacene spectrum which is greater than the effect of two phenyl groups in other, but equivalent, positions demonstrates that the π -electron systems of the phenyl groups, although perpendicular to that of the naphthacene, interact with the latter. A plausible mechanism for such an interaction of two perpendicular π -electron systems has been suggested. It consists of the interaction of the molecular (or group) orbitals of each of the two groups which have, in addition to their own essential nodal plane, a nodal plane coincident with the essential nodal plane of the other portion of the molecule. Alternatively, the interaction is introduced by failing to make the usual assumption of neglecting all non-neighboring resonance integrals. This model leads immediately to a bathochromic effect of one π -electron system on the other. On the basis of this model, it is impossible to decide whether the bathochromic effect of a phenyl substituent in naphthacene is due to ordinary resonance interaction, or exclusively to the interaction postulated here. At the same time, the demonstration of the possibility of such interaction indicates that calculations of angles of twist in non-planar π -electron systems² may be affected by a considerable error. Since the completely twisted compound would absorb at longer wave length than anticipated in the models commonly used, angles so calculated are likely to be an underestimate. However, the uncertainties introduced by this factor are probably no greater than those caused by some of the other assumptions made.

Once a possible mechanism for the interaction of perpendicular π -electron systems is established, the bathochromic effect of two parallel phenyl groups on the naphthacene is readily established, using a reasonable, although exceedingly crude, model. The additional bathochromic effect caused by introduction of two pairs of neighboring phenyl groups is explained as a steric constraint approaching the phenyl groups. Data on other naphthacene derivatives are in essential agreement with arguments presented.

It appears conceivable that the experimental results might also be explained by the local excited state-electron transfer state model.³ A detailed treatment, however, seems exceedingly difficult, particularly if the interactions of the parallel phenyl rings are to be included.

Finally it may be worthwhile to point out that the importance of non-neighboring resonance integrals very likely is a rather general phenomenon, and probably plays a considerable role in such phenomena as homoconjugation.

Acknowledgments.—The authors wish to acknowledge several interesting discussions with Profs. J. Rigaudy and R. Daudel, which stimulated this work and helped to clarify the ideas presented.