energy than quinazoline; while quantitative data are lacking, the nitrogen-containing ring of quinoxaline certainly seems to be more labile to hydrolysis than that of quinazoline.

The resonance energies predicted for oxygen compounds also seem to be consistent with their chemical behavior; thus the resonance energies of benzaldehyde, the hydroxybenzenes, and phenyl ketones are predicted to be not dissimilar to that of benzene, and the naphthols to that of naphthalene. The enhanced acidity of the phenols can of course be attributed to an increase in resonance energy when the group adjacent to phenyl or naphthyl is $O^-$ instead of OH, $O^-$ being much less electronegative.

On the other hand the calculated resonance energies lead to the prediction that three compounds, normally considered aromatic, in fact are not, *viz.*, furan, tropone, and tropolone. This, however, seems to be consistent with the available data.

The bond lengths in furan[14a] are very similar to those that would be predicted for a 1,3-butadiene derivative,[14b] and the classical nature of this molecule is further supported by the facility with which it undergoes Diels–Alder reactions, unlike thiophene or pyrrole. The chemical reactions of furan are also exactly what would be expected for a cyclic dienyl ether; substitution reactions take place only in cases where electrophilic attack on furan would lead to an intermediate carbonium ion that might be expected to undergo loss of a proton rather than addition, in order to avoid forming a product with eclipsed $sp^3$ carbon atoms.

The conclusions regarding tropone and tropolone are perhaps more startling, since the aromatic nature of tropolone was a presupposition of its original postulation as a component of stipitatic acid and colchicine.[15] However, most of the special properties of these compounds can be attributed to the facility with which they form symmetrical conjugate acids or bases, rather than to any special properties of the parent compounds. Thus tropone is very stable under acidic conditions, when it exists as the conjugate acid $C_7H_6OH^+$, but not under neutral or basic conditions, when it can undergo, *e.g.*, Diels–Alder reactions,[16] whereas tropolone, which can exist both as a stable conjugate acid, dihydroxytropylium, $C_7H_5(OH)_2^+$, and as a stable conjugate base, $C_7H_5O_2^-$, is stable to both acids and bases.

Further confirmation is provided by a recent structure determination for 4,5-benzotropone[17] which shows the seven-membered ring in this compound to have a classical structure, the lengths of the "single" and "double" carbon–carbon bonds being close to those in 1,3-butadiene.

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[14] (a) B. Bak, L. Hansen, and J. Rastrup-Andersen, *Discussions Faraday Soc.*, **19**, 30 (1955); (b) M. Traetteberg, *Acta Chem. Scand.*, **22**, 628 (1968), and references therein.

[15] M. J. S. Dewar, *Nature*, **155**, 50, 141, 479 (1945).

[16] S. Ito. Y. Fujise, and M. C. Woods, *Tetrahedron Lett.*, 1059 (1967); S. Ito, Y. Fujise, and M. Sato, *ibid.*, 691 (1969).

[17] T. Hata, H. Shimanouchi, and Y. Sasada, *ibid.*, 753 (1969).

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# A Critical Evaluation of the Dependence of $^3J_{\mathrm{HH}}$ Couplings on Bond Order and Bond Length in Conjugated Carbocyclic Molecules. Evidence for a Steric Effect on $^3J_{\mathrm{HH}}$[1]

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*Received June 2, 1969*

**Abstract:** Previously proposed linear correlations between π-bond orders and the magnitudes of nmr *ortho* proton–proton spin–spin coupling constants ($^3J$) in unsaturated systems have been reinvestigated using more accurate values for the coupling constants than were available heretofore. It is shown that, although the relationship is no longer linear over the whole range of bond order, the plot is still approximately linear for aromatic systems. Deviations from linearity are shown to exhibit consistent trends, which may be rationalized in terms of steric interactions. A plot of $^3J$ *vs.* bond length is shown to be linear over the whole range of bond lengths, and the theoretical background of this correlation is discussed in terms of a simple molecular orbital theory, as well as a previously proposed valence bond treatment.

Apart from their invaluable aid in structural studies, determinations of reliable nuclear magnetic resonance (nmr) spin–spin coupling constants provide a criterion against which molecular wave functions and theoretical treatments can be tested. However, while high-resolution nuclear magnetic resonance (nmr) spectra have been recorded for more than a decade, it is only more recently, with the advent of iterative computer fitting of spectra and field-frequency locked spectrometers operating at high field strengths, that many complex spin systems have become amenable to complete analysis. In connection with another project, we had occasion to remeasure the spectra of some aromatic and olefinic compounds. In several cases we obtained vic-

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[1] This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

[2] NASA Resident Research Associate, 1968–1969.

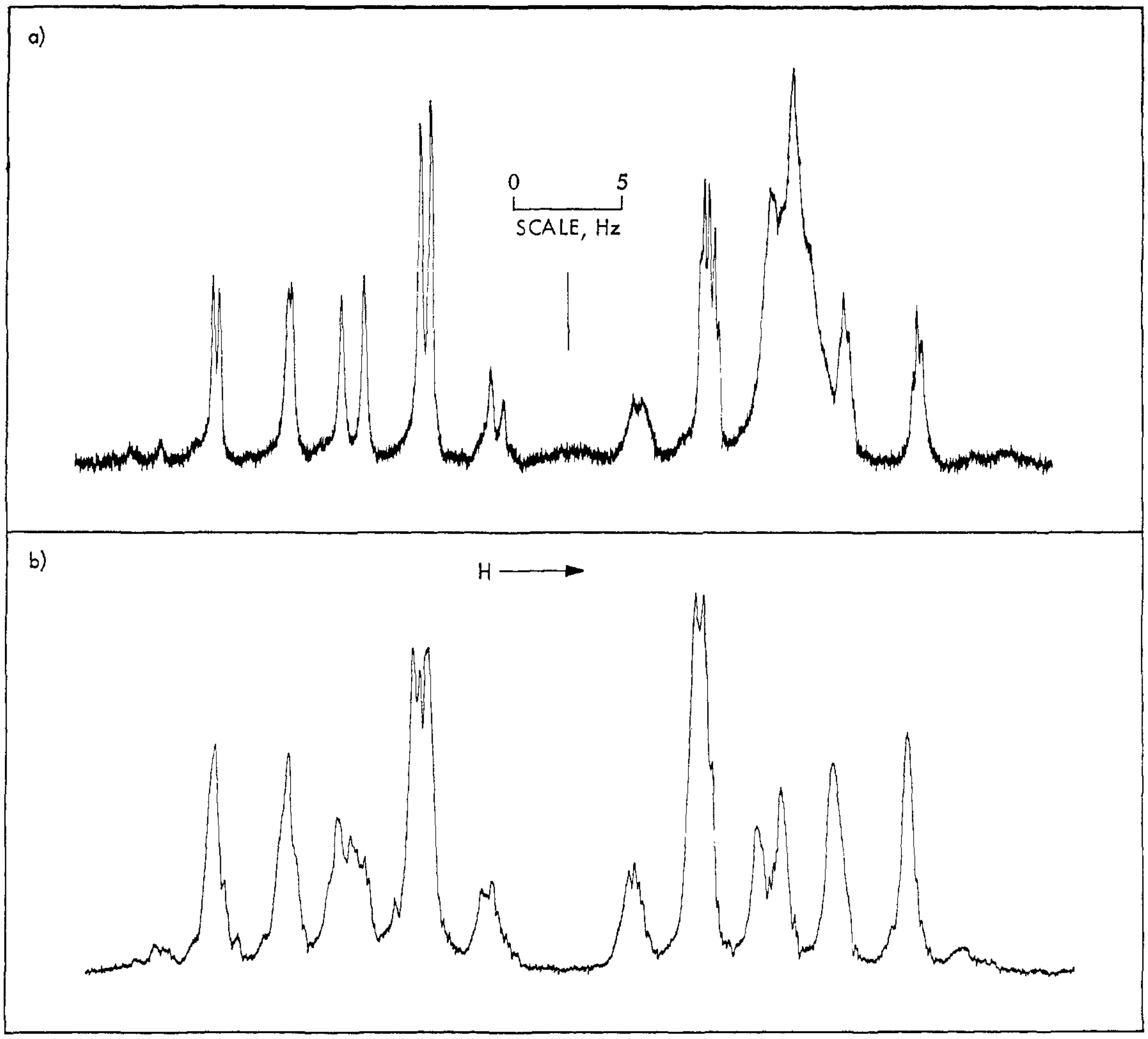

Figure 1. The nmr spectrum of 1,4-dideuterionaphthalene (a) and naphthalene (b), taken at 60 MHz in $CCl_4$ solution.

inal vinyl or aromatic coupling constant (HC=CH) values deviating significantly from previously reported results. These observations prompted us to recheck our work carefully and reinvestigate the spectra of a number of additional members of these classes of molecules. In this report, we present these new data. The interpretation of the variations in magnitudes of these coupling constants with molecular structure described below has allowed for the first time the clear identification of the contributions of certain specific steric interactions to these couplings.

Some time ago, and before the advent of computer programs for the fitting of spectra, Jonathan, *et al.*,[3] performed analyses of some of the compounds studied by us. Although certain of their analyses were only approximate, they were able to demonstrate a correlation between the magnitudes of the *ortho* proton–proton coupling constant ($^3J$) in these compounds and the Hückel $\pi$-bond order ($p_{ij}$) of the corresponding bond. Later, other workers[4,5] added further points to this correlation. More recently Smith, *et al.*,[6] extended this relationship to include charged aromatics in both the five- and six-membered ring series. Smith's correlation for the six-membered series exhibited appreciable scatter in the points, *viz.* a root mean square (rms) error in the fit of 0.27 Hz. We were particularly interested to see whether this was due to experimental error in the data, or whether systematic deviations from the correlation were in fact occurring. It appears that the latter is the case, and a correlation of a rather different form is proposed in which structure-dependent terms are included. A further correlation between $^3J$ and bond length is also demonstrated, and it is shown that this may be put on a reasonably satisfactory approximate theoretical basis using a simple molecular orbital treatment. This approach, we feel, possesses useful diagnostic and intuitive features, which may be used with advantage over more sophisticated theoretical descriptions. This is not to deny, of course, the fundamental importance of more complete theoretical treatments of the couplings in these systems such as have recently been published.[7] Indeed it is hoped that the present work, in presenting more accurate experimental values, will serve to stimulate further theoretical work on the correlation of nmr parameters with molecular structure.

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(3) N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, 36, 2443 (1962).

(4) R. C. Fahey and G. C. Graham, *J. Phys. Chem.*, 69, 4417 (1965).

(5) J. D. Memory, G. W. Parker, and J. C. Halsey, *J. Chem. Phys.*, 45, 3567 (1966).

(6) W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Am. Chem. Soc.*, 89, 1438 (1967).

(7) See M. A. Mainster and J. D. Memory, *J. Chem. Phys.*, 49, 3992 (1968), and references therein.

## Experimental Section

Spectra were recorded on Varian A-56/60 and (more commonly) HA-100 instruments. No attempt was made to employ a constant concentration or standard solvent throughout the work; hence the derived chemical shifts are not suitable for systematic investigation.[3,5]

Calibration of the spectra was by direct frequency count (HA-100) or the audio side band method (A-56/60) with approximately one calibration per 5 Hz. The maximum sweep expansion was used for measured spectra, and transition frequencies used were the mean of at least three spectra. In all cases the rms error of the transition frequencies was 0.05 Hz or less.

In certain cases, inter-ring couplings broaden the transitions of interest; this results in coupling constants having large probable error ranges. Where possible, therefore, we have overcome this by one of two methods. First, in the important case of naphthalene, the 1,4-dideuterio compound was used; the 5,8-protons in this system give rise to the sharp signals in the downfield region. Sufficient sharp lines (from the 6,7-protons) could be picked out in the upfield region to enable an accurate chemical shift difference to be determined (*cf.* Figure 1). Second, *e.g.*, anthracene, decoupling the broad 9,10-proton singlet gave sharper lines in the AA′BB′ system.

## Spectral Analyses and Results

The assignments of the spectra have been given by other workers,[3,5] or else will be given later.[8] The coupling constants and chemical shifts are given in Table I, together with information on the solvents used.

In certain of the molecules there exist couplings which can only be extracted from the separation between rather broad peaks (*ca.* 1–2 Hz width at half-height). These were not used directly in the correlation, but are discussed later (see Table II).

The couplings between protons 3,4 and 9,10 in pyrene and phenanthrene were extracted from the $^{13}C$ satellite signals. Because of the restricted solubility of these compounds, the satellites had to be recorded with the aid of the Varian C-1024 computer of average transients (CAT), calibrated immediately prior to recording the satellite by scanning a single pass of a spectrum which was sufficiently strong to be calibrated directly on the spectrometer. Further, the reference spectrum was arrayed by means of the spectrometer offset to occur in the same (central) position of the sweep as did the satellite spectrum.

The value for cyclohexene was obtained by decoupling the signal of the adjacent methylene groups, and then recording the $^{13}C$ satellite signals of the olefinic protons in natural abundance. These occur as a pair of sharp doublets, and the coupling may be extracted directly.

In all cases, the parameters for spin systems with three or more nuclei have been derived by iterative computer techniques using the programs NMRENIT[9] or more commonly LAOCN-3.[10] In many of the spectra recorded in our work, *e.g.*, the $AB_2$ analysis of pyrene or the AA′BB′ spectra of napthalene and anthracene, the coupling constant and chemical shift parameters may be extracted directly from the spectra. Nonetheless, we believe that use of the computer method throughout is more consistent. As well as having the advantage of providing a set of errors for the parameters, this approach utilizes all the available experimental line positions. These parameter set errors, as well as the rms error of the fit of line positions, are quoted in Table I.

The significance of the parameter set error of LAOCN-3 is not entirely clear; *e.g.*, Castellano[11] has suggested that these errors need to be multiplied by a factor of ~5 to provide a realistic estimate of the errors. On this basis, our coupling constants are considered good to approximately 0.05–0.1 Hz except where otherwise indicated.

In an attempt to substantiate this estimate, the spectrum of 1,4-dideuterionaphthalene was taken at both 60 and 100 MHz, while two separate sets of spectra of triphenylene taken at 100 MHz were analyzed. The results are included in Table I. It can be seen that in the case of naphthalene, where all 12 lines in the low-field region may be resolved, the two sets are in agreement to within 0.025 Hz, whereas in the case of triphenylene, where the spectrum is more degenerate (tending toward an AA′XX′ system), and inter-ring couplings render the lines rather broad (*ca.* 0.6-Hz line width at half-height as compared to a TMS line width of *ca.* 0.3 Hz), the two sets agree to only 0.05 Hz. Hence Castellano's suggestion[11] seems slightly pessimistic, although the actual factor may well depend on the symmetry of the system. Short comments on the analyses of previous workers are given, where pertinent.

**Cyclohexene.** Smith and Kriloff[12] quoted 8.8 Hz, from an analysis of the olefinic splitting pattern, but admitted an imperfect fit with the observed. Laszlo and Schleyer,[13] with the aid of the CAT, obtained 9.6 Hz from the $^{13}C$ satellite spectrum of the olefinic protons. It is not stated by these authors whether the CAT sweep was calibrated. The present results, being calibrated directly on the spectrometer, are felt to be accurate to ±0.05 Hz.

**1,3-Cyclohexadiene.** The details of this analysis will be reported shortly.[8]

**Benzene.** The results of Goldstein's[14] analysis of the $^{13}C$ satellite spectrum are given. These values are in excellent agreement with the extrapolations made by Castellano.[15]

**1,2-Dihydronaphthalene.** The value for $J_{12}$ is from our analysis which will be published shortly.[8]

**Naphthalene.** Previous analyses either assumed $J_{14} = 0$, *e.g.*, ref 3, or else seem to be inaccurate because of poor resolution—*e.g.*, Lim, *et al.*,[16] record only eight lines in each half. Use of the dideuterio compound enables 12 lines in the low-field half to be resolved (Figure 1a).

**Phenalene.** We are indebted to Dr. U. Scheidegger for providing us with information on this analysis.[17]

**Anthracene.** The spectrum was recorded with the 9,10-protons decoupled. The previous analysis[3] took $J_{14} = 0$ Hz.

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(8) M. A. Cooper, D. D. Elleman, and S. L. Manatt, to be published.

(9) M. T. Bowers, T. I. Chapman, and S. L. Manatt, *J. Chem. Phys.*, 50, 5412 (1969); this program is a modification and combination of NMREN-2 and NMRIT, originally described by J. D. Swalen and C. A. Reilly, *ibid.*, 37, 21 (1962).

(10) An improved version of LAOCOON II: S. M. Castellano and A. A. Bothner-By, *ibid.*, 41, 3863 (1964). We are indebted to Professor Castellano for a listing and description of this program.

(11) S. M. Castellano, C. Sun, and R. Kostelnik, *Tetrahedron Letters*, 5205 (1967).

(12) G. V. Smith and H. Kriloff, *J. Am. Chem. Soc.*, 85, 2016 (1963).

(13) P. Laszlo and P. von R. Schleyer, *ibid.*, 85, 2017 (1963).

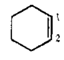
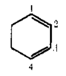
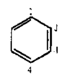
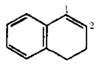
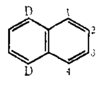
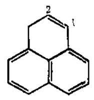
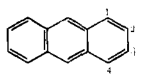
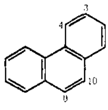
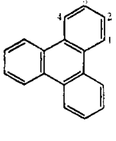
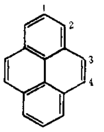
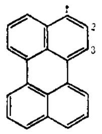
(14) J. M. Read, R. E. Mayo, and J. H. Goldstein, *J. Mol. Spectrosc.*, 21, 235 (1966).

(15) S. M. Castellano and C. Sun, *J. Am. Chem. Soc.*, 88, 4741 (1966).

(16) T. K. Lim, A. Taurins, and M. A. Whitehead, *Can. J. Chem.*, 44, 1211 (1966).

(17) H. Prinzbach, V. Freudenberger, and U. Scheidegger, *Helv. Chim. Acta*, 50, 1087 (1967).

**Table I.** The Nmr Spectral Parameters of Some Aromatic Systems

| Compd | Compd no. | i,j | $J_{ij}$,[a] Hz | Chemical shift,[a,b] Hz | Bond length Å, | | Solvent | Rms error |
|---|---|---|---|---|---|---|---|---|
| | | | | | $p_{ij}$[c] | ($R_{ij}$) | | |
|  | **1** | 1,2 | 10.11 ± 0.05 | 1 558.1 | 1.000 | 1.335[d] | 50% in $CCl_4$ | |
|  | **2** | 1,2 | 9.64 (0.006) | 1 568.31 (0.005) | 0.894 | 1.339[e] | $C_6H_6$ | 0.016 |
| | | 1,3 | 1.02 (0.005) | 2 582.89 (0.005) | | | | |
| | | 1,4 | 1.12 (0.007) | | | | | |
| | | 2,3 | 5.04 (0.007) | | 0.447 | 1.468[e] | | |
|  | **3** | 1,2 | 7.56 ± 0.05 | | 0.667 | 1.397[f] | ($C_6H_6$) | 0.055 |
| | | 1,3 | 1.38 ± 0.05 | | | | | |
| | | 1,4 | 0.68 ± 0.05 | | | | | |
|  | **4** | 1,2 | 9.56 (0.017) | 1 632.50 (0.012) | 0.911 | | $CCl_4$ | 0.039 |
| | | | | 2 581.82 (0.012) | | | | |
|  | **5** | 1,2 | 8.30 (0.012) | 1 460.81 (0.007) | 0.724 | 1.368[g] | $CCl_4$ (60 MHz) | 0.028 |
| | | 1,3 | 1.20 (0.010) | 2 439.35 (0.007) | | | | |
| | | 1,4 | 0.74 (0.009) | | | | | |
| | | 2,3 | 6.83 (0.010) | | 0.603 | 1.414[g] | | |
| | | 1,2 | 8.29 (0.013) | 1 767.35 (0.007) | 0.724 | 1.368[g] | $CCl_4$ (100 MHz) | 0.031 |
| | | 1,3 | 1.22 (0.013) | 2 731.63 (0.007) | | | | |
| | | 1,4 | 0.76 (0.010) | | | | | |
| | | 2,3 | 6.86 (0.012) | | 0.603 | 1.414[g] | | |
|  | **6** | 1,2 | 9.6 ± 0.05 | 1 649 | 0.899 | | $CCl_4$ | |
| | | | | 2 588 | | | | |
|  | **7** | 1,2 | 8.54 (0.018) | 1 798.89 (0.007) | 0.737 | 1.379[h] | $CDCl_3$ | 0.027 |
| | | 1,3 | 1.14 (0.018) | 2 744.19 (0.007) | | | | |
| | | 1,4 | 0.70 (0.015) | | | | | |
| | | 2,3 | 6.60 (0.017) | | 0.586 | 1.419[h] | | |
|  | **8** | 1,2 | 8.00 (0.016) | 1 766.33 (0.007) | 0.707 | 1.381[i] | $CS_2$ | 0.027 |
| | | 1,3 | 1.37 (0.015) | 2 739.29 (0.011) | | | | |
| | | 1,4 | 0.62 (0.011) | 3 742.69 (0.011) | | | | |
| | | 2,3 | 7.00 (0.010) | 4 842.08 (0.008) | 0.623 | 1.398[i] | | |
| | | 2,4 | 1.28 (0.019) | | | | | |
| | | 3,4 | 8.26 (0.018) | | 0.702 | 1.383[i] | | |
| | | | | 9 751.09 | | | | |
|  | **9** | 1,2 | 8.40 (0.023) | 1 850.58 (0.009) | 0.690 | 1.377[j] | $CS_2$ | 0.033 |
| | | 1,3 | 1.34 (0.023) | 2 753.31 (0.009) | | | | |
| | | 1,4 | 0.54 (0.021) | | | | | |
| | | 2,3 | 6.88 (0.017) | | 0.637 | 1.402[j] | | |
| | | 1,2 | 8.36 (0.025) | 1 850.57 (0.009) | 0.690 | 1.377[j] | $CS_2$ | 0.037 |
| | | 1,3 | 1.30 (0.025) | 2 753.30 (0.009) | | | | |
| | | 1,4 | 0.50 (0.023) | | | | | |
| | | 2,3 | 6.92 (0.019) | | 0.637 | 1.402[j] | | |
|  | **10** | 1,2 | 7.72 (0.013) | 1 775.14 (0.014) | 0.669 | 1.380[k,l] | $CS_2$ | 0.027 |
| | | | | 2 790.45 (0.012) | | | | |
| | | | | 3 779.6 | | | | |
|  | **11** | 1,2 | 8.15 (0.019) | 1 755.41 (0.015) | 0.707 | 1.370[m] | $CS_2$ | 0.028 |
| | | 1,3 | 0.99 (0.020) | 2 736.81 (0.015) | | | | |
| | | 2,3 | 7.48 (0.020) | 3 803.65 (0.014) | 0.629 | 1.418[m] | | |

[a] Parameter set errors from LAOCN-3 are enclosed in parentheses; values indicated thus "±0.05" are obtained directly from a spacing. [b] In hertz, downfield from internal TMS at 100 MHz except where stated. [c] Values taken from ref 25. [d] J. F. Chiang and S. H. Bauer, *J. Am. Chem. Soc.*, **91**, 1898 (1969). [e] G. Dallinga and L. H. Toneman, *J. Mol. Structure*, **1**, 11 (1968). [f] "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958. [g] S. C. Abrahams, J. M. Robertson, and J. G. White, *Acta Cryst.*, **2**, 233 (1949). [h] A. McL. Mathieson, J. M. Robertson, and V. C. Sinclair, *ibid.*, **3**, 245 (1950). [i] J. Trotter, *ibid.*, **16**, 605 (1963). [j] F. R. Ahmed and J. Trotter, *ibid.*, **16**, 503 (1963). [k] A. Camerman and J. Trotter, *ibid.*, **18**, 636 (1965). [l] I. Ikemoto and H. Kuroda, *ibid.*, **B24**, 383 (1968). [m] A. Camerman and J. Trotter, *Proc. Roy. Soc.* (London), **A279**, 129 (1964).

**Phenanthrene.** The analysis of Batterham, *et al.*,[18] assumed $J_{12} = J_{34}$, and $J_{14} = 0.5$ Hz. That of Fahey, *et al.*,[4] agrees (±0.1 Hz) with the coupling constants found in the present work.

**Pyrene.** Jonathan, *et al.*,[3] obtained parameters from the $AB_2$ analysis very close to the present ones.

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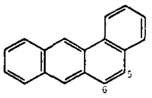
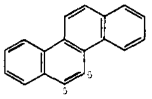
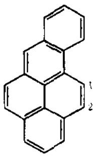
(18) T. J. Batterham, H. Tsai, and H. Ziffer, *Australian J. Chem.*, 18, 1959 (1965).

Table II. Certain Less Accurate Couplings Obtained by Partial Analysis of Some Aromatic Systems and a Test of Equation 3

| Molecule | Compd no. | $i,j$ | $p_{ij}$ | $R_{ij}$, Å | $J_{ij}$ (±0.2 Hz) | Calcd Eq 1 | Calcd Eq 3 |
|---|---|---|---|---|---|---|---|
|  | **8** | 9,10 | 0.775 | 1.372[a] | 9.0 | 8.88 | 9.01 |
|  | **10** | 3,4 | 0.777 | 1.32,[b] 1.42[c] | 8.8 | 8.90 | 9.03 |
|  | **12** | 5,6 | 0.783 |  | 9.0 | 8.97 | 9.10 |
|  | **13** | 5,6 | 0.754 | 1.369[d] | 9.1 | 8.63 | 8.99 |
|  | **14** | 1,2 | 0.754 |  | 9.05 | 8.63 | 8.99 |

[a] J. Trotter, *Acta Cryst.*, **16**, 605 (1963). [b] A. Camerman and J. Trotter, *ibid.*, **18**, 636 (1963). [c] I. Ikemoto and H. Kuroda, *ibid.*, **B24**, 383 (1968); values *b* and *c* show a large discrepancy, and both seem rather unlikely. [d] D. M. Burns and J. Iball, *Proc. Roy. Soc.* (London), **A257**, 491 (1960).

**Triphenylene.** Jonathan, *et al.*,[3] assumed, incorrectly, that $J_{14} = 0$.

**Perylene.** Jonathan, *et al.*,[3] analyzed this as an ABX system, whereas in the present work an ABC analysis was used. Taking their reported transition frequencies and recalculating as an ABC system give values within 0.1 Hz of the present.

Partial analyses of benzanthracene and chrysene have been reported by other workers.[5] All that has been done in our work is to remeasure the splittings which yield the couplings directly of interest to us. No analysis of the benzopyrene (**14**) appears to have been made. The quoted coupling is the spacing of the doublet at low field—tentatively assumed to be that of proton 1, by analogy with ref 5 (see Table II).

## Discussion

Having obtained these new data, we were interested to see how well the proposed linear correlations[3,6] between $^3J$ and the Hückel π-bond orders ($p_{ij}$) were followed. However, in testing any correlation, it is necessary to make every effort to exclude extraneous effects. Our attempts to do this are discussed here in some detail.

It has been demonstrated[19] in acyclic systems that $^3J$ is very sensitive to the electronegativity of substituents, while in cyclic systems it is sensitive to ring size[12,13,20] and, therefore, presumably to angle strain. Castellano[21] has demonstrated the effect of strain between *ortho* substituents on the ring couplings in various benzenes. For this reason, we believe it unwise to include, as did Smith, *et al.*,[6] the values for strained molecules such as biphenylene in the correlation. In an attempt to minimize strain effects, we have selected only molecules composed entirely of six-membered carbocycles. Order of magnitude calculations for the residual effect of angle strain are made later. Again, Castellano[15] has demonstrated correlations between couplings in monosubstituted benzenes and the substituent electronegativity. Hence, it might be expected that in going from benzene to naphthalene, there would be a change in the couplings due to replacing a proton by a more electronegative carbon atom, as well as the effect due to changes in bond order. Fortunately, it appears that the effect of such a replacement, *e.g.*, by $CH_3$, is very small,[22] and the good correlation which will be demonstrated between $^3J$ and $p_{ij}$ further suggests that this can be ignored.

The Hückel MO method is a gross oversimplification but it has been applied with fair success, particularly to alternate hydrocarbons.[23,24] It may well be significant that all compounds used here can be considered as members of this class. The Huckel π-bond orders were directly from a compilation of simple molecular orbital functions.[25] Thus 1,3-cyclohexadiene (**2**) and 1,2-dihydronaphthalene (**4**) are approximated as 1,3-butadiene and styrene, respectively. It might be argued that use of these simple Huckel bond orders is too drastic an oversimplification and that, for example, a self-consistent (SCF) procedure[23,24] should be used to obtain these. This has not been done for two reasons. First, for an empirical correlation, the method of obtaining the bond order should be relatively unimportant and the Huckel method is simple and well defined, whereas in the case of many SCF methods, the added complications tend to detract from clear general intuitive understanding of the situation. Second, and as discussed more fully below, the correlation is not of primary theoretical significance; hence there would seem to be little point in trying to include undue theoretical refinements in it. However, for charged systems, and those containing heteroatoms, Smith, *et al.*,[6]

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(19) For a recent discussion, see T. Schaefer and H. M. Hutton, *Can. J. Chem.*, **45**, 3153 (1967).

(20) O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963).

(21) S. M. Castellano and R. Kostelnik, *Tetrahedron Letters*, 5211 (1967).

(22) M. P. Williamson, R. Kostelnik, and S. M. Castellano, *J. Chem. Phys.*, **49**, 2218 (1968).

(23) See, among others, A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961.

(24) "Molecular Orbital Theory of Conjugated Systems," L. Salem, W. A. Benjamin, Inc., New York, N. Y., 1966.

(25) "Supplementa lTables of Molecular Orbital Calculations, with a Dictionary of π-Electron Calculations," J. I. A. Streitwieser, and Brauman, C. A. Coulson, and A. Streitwieser, respectively, Pergamon Press, Oxford, 1965.

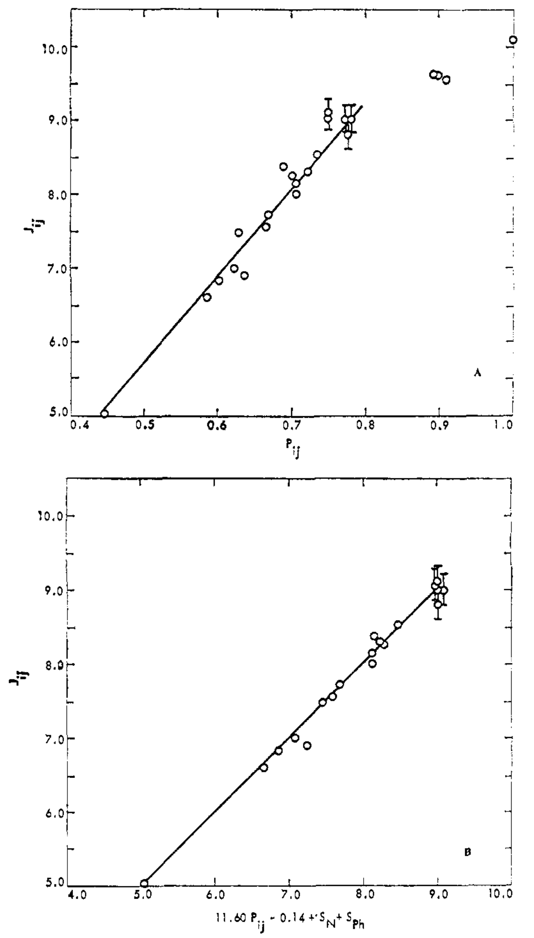


Figure 2. Plots of $^3J$ *vs.* $p_{ij}$: A, plot of all data where the solid line represents the correlation given by eq 1; **B**, plot of data for aromatic $p_{ij}$'s where the solid line represents the correlation given by eq 3.

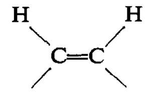
have demonstrated the usefulness of a (SCF) method using an $\omega$ technique.[23,24] Surprisingly, however, they used only the Hückel bond orders for 1,3-cyclohexadiene.

The plot of $^3J$ *vs.* $p_{ij}$ is shown in Figure 2A, and it is seen that with these accurate new data there is considerable curvature, *which is not due to experimental error.* However, for $0.4 < p_{ij} < 0.8$, *i.e.*, for those bonds usually considered[26] to be "aromatic" in character, the relation

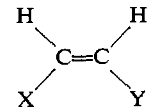
$$^3J = 11.75p_{ij} - 0.23 \qquad (1)$$

is followed with an rms deviation of 0.15 Hz. The less accurate data in Table II have not been used in deriving eq 1.

At this stage we consider first whether the curvature in the plot can be ascribed to violation of one or more of the criteria for inclusion discussed previously. Points having $p_{ij} > 0.8$ are for compounds having one or more sp$^3$-hybridized carbons attached to the molecular fragment, in contrast to the sp$^2$ carbons found for



$p_{ij} < 0.8$. Now an sp$^2$ carbon is more electronegative than an sp$^3$ carbon atom (2.74–2.50 on the Pauling scale).[27] A recent empirical correlation[19] between $^3J_{cis}$ in the fragment

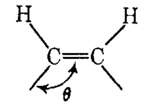


and the Pauling electronegativities ($E_X$, $E_Y$) of X and Y has yielded the equation

$$^3J_{cis} = \frac{91.2}{E_X + E_Y} - 9.7 \qquad (2)$$

We can calculate that $^3J$ in cyclohexene should be reduced by about 1.6 Hz to compensate for this effect. Such a correction would emphasize the deviation from linearity in Figure 2A even more.

Second, we consider the effect of slight bond angle changes on these couplings. In cyclohexene and cyclopentene we have measured couplings of 10.11 and 5.57 Hz, respectively, for values[28,29] of the angle $\theta$ in the fragment



of 123.3 and 111.5°. If we assume a linear correlation between $^3J$ and $\theta$ in this angle range, the value of $^3J$ would be approximately 8.8 Hz in a hypothetical cyclohexene having $\theta = 120°$ (*i.e.*, that angle found in benzene and presumably the other aromatics taken here). Again the correction would be in the wrong direction to allow for the curvature. Hence we conclude that there is no simple way of removing the bend from the plot in Figure 2A.

Equation 1 is capable of correlating the data in the linear region to an accuracy of ±0.15 Hz. We now show that this magnitude of deviation arises from systematic sources which can be reasonably described by the presence of steric effects on proton–proton couplings. In Figure 2A it can be seen that only four points exhibit a deviation from eq 1 of more than twice the rms error. In the three of these deviations occurring above the plot, one of the coupled protons could reasonably suffer significant steric interaction with a neighboring proton of the "phenanthric" type (Figure 3a). It is well known that these protons exhibit large downfield compressional chemical shifts.[30] The two effects may be related and we suggest that the deviations in Figure 2A for phenanthrene (**8**), perylene (**11**), and triphenylene (**9**), which are *ca.* 0.3 Hz larger than predicted by eq 1, arise from a steric origin. The deviation in the opposite direction for $J_{23}$ in triphenylene is not understood. Possibly this is connected with the fact that triphenylene is the only molecule considered here in which one aromatic ring is subjected to two interactions of the "phenanthric" type. A similar but rather smaller effect occurs when one of the coupling nuclei suffers an interaction of the "naphthalenic" type

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[26] See ref 23, p 172.

[27] G. Pilcher and H. A. Skinner, *J. Inorg. Nucl. Chem.*, **24**, 937 (1962).

[28] L. H. Scharpen, J. E. Wollrab, and D. P. Ames, *J. Chem. Phys.*, **49**, 2368 (1968).

[29] G. W. Rathjens, *ibid.*, **36**, 2401 (1962).

[30] For the most recent discussion of this, see B. V. Cheney, *J. Am. Chem. Soc.*, **90**, 5386 (1968).

(Figure 3b), and molecules where this interaction exists tend to have couplings averaging 0.1 Hz larger than those without the interaction (for the same $p_{ij}$ value). A survey of the results available for the chemical shifts in the corresponding cases, *e.g.*, using results in ref 5, fails to reveal any anomalies in the shifts. Possibly the theory of chemical shifts in these systems is insufficiently developed for this effect to show up.

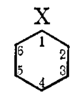
Having discovered these consistencies in the effect of structural features on the couplings, we are led to propose the new correlation

$$^3J = 11.60p_{ij} - 0.14 + S_N + S_{Ph} \qquad (3)$$

where $^3J$, $p_{ij}$ have the same meaning as before, and $S_N$, $S_{Ph}$ are factors dependent on structure. If one (or both) of the coupling protons suffers an interaction of the "naphthalenic" or "phenanthric" types, then one (or two) of the respective contributions $S_N$, $S_{Ph}$ must be added. With $S_N = +0.08$ Hz, $S_{Ph} = +0.30$ Hz, the present data are reproduced with an rms deviation of 0.08 Hz (see Figure 2B), which is more nearly comparable with the experimental error in the measured coupling constants. The most critical distinction between eq 1 and 3 occurs in larger molecules, where both of the steric interactions may be operating on the coupling system. However, it is in just these molecules that the couplings are of lesser accuracy, so the test is not completely decisive. The results found in some of the polycyclic compounds are shown, together with the values predicted by eq 1 and 2, in Table II. Where a distinction seems possible, *e.g.*, in chrysene (**13**) and benzpyrene (**14**), eq 3 seems more accurate.

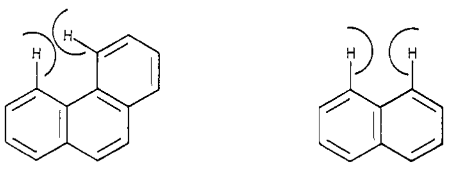
The high degree to which eq 3 reproduces the experimental data seems to imply that the couplings are indeed modified by steric factors. However, the deduction of such an effect from deviations on an empirical correlation (eq 1) is hardly the most compelling evidence, and work is in hand to test this hypothesis. Two pieces of evidence which seem to support our proposal are quoted here.

Results of the analyses of toluene[22] and *t*-butylbenzene[21] are available and we consider that these exhibit the effect of strain on the protons *ortho* to the bulky substituent. This is most clear in the couplings $J_{23}$



(7.96 and 7.64 Hz for X = *t*-Bu and $CH_3$, respectively) and $J_{26}$ (2.18 and 1.86 Hz, respectively). (Note that the magnitude of the enhancement of $J_{23}$ is very similar to that produced by a phenanthric interaction, which is reasonable since molecular models show the compressed protons suffer comparable interactions in the two cases.) The other differences are much smaller. However, the observed differences could also be accounted for if the *t*-Bu group was rather more electronegative[15] than Me. To account in this manner for the difference in $J_{23}$, the *t*-Bu group would have to be more electronegative than Me by *ca.* 0.6 Pauling electronegativity unit, which seems rather unlikely.

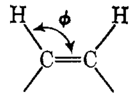
Second, we have analyzed the spectrum of 1,4-di-*t*-butylnaphthalene[31] and find a value for $J_{56}$ of 8.88 Hz which is substantially larger than the corresponding value in the unsubstituted compound (8.30 Hz). Here again it is most unlikely that the effect could be ascribed to electronegativity.



(a) (b)

Figure 3. Phenanthric (a) and naphthalenic (b) interactions.

The reason for the increase in $^3J$ when one of the protons is in the configurations shown in Figure 3 does not seem clear. At first sight, it is tempting to ascribe this to reductions in the angles $\phi$ of the coupling system shown below. Thus in cyclohexene and cyclopentene,



respectively, $\phi = 118.4$ and 124.2° (see the arguments presented above for $\theta$), and therefore a decrease of less than a degree in $\phi$ could account for the observed changes in couplings.[32] Considerable work[33] has been done on the distortion of polycyclic aromatic compounds under the influence of molecular overcrowding. The magnitude of the in-plane bending in molecules containing phenanthric interactions has been estimated[33b] as *ca.* $\phi = 2°$, but the results of these calculations could not be fully checked against experiment, since the X-ray method is not sensitive enough to show up such small angle changes. Certainly the published structures (footnote to Table I) exhibit no consistency in C=CH angles which would be expected to be equal in the absence of packing forces.[33a] In his discussion of proton compressional shifts, Cheney[30] proposed a model "involving sterically induced charge polarization in the H-C bond." This charge redistribution may well also affect the proton-proton coupling, as would any out-of-plane bending. Further theoretical and experimental information is needed to settle this point.

Trends in $^4J$ and $^5J$ in the aromatics are less easily found. The latter is remarkably constant (0.50–0.75 Hz), while it is perhaps noteworthy that in the series benzene, naphthalene, anthracene, successive annelations produce a decrease in $^4J$.

It was recognized by Jonathan, *et al.*,[3] that their correlation did not necessarily imply that the coupling was transmitted *via* the $\pi$-electron system. In particular calculations by McConnell[34] have indicated the $\pi$-electron contribution to $^3J$ is $\lesssim 1$Hz. It was suggested that[3] "the variation of bond-order is presumably accompanied by an accompanying change in the distance of proton–proton separation, so that the change in spin-spin coupling constant may be due to changes in the amount of delocalization produced by orbital overlap."

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[31] R. W. Franck and K. Yanagi, *J. Org. Chem.*, 33, 811 (1968); we should like to thank Professor Franck for loaning us his sample.

[32] M. Karplus [*J. Am. Chem. Soc.*, **85**, 2870 (1963)] has considered this problem in the aliphatic H–C–C–H fragment in terms of a valence bond approach.

[33] (a) For a review, see G. Ferguson and J. M. Robertson, *Advan. Phys. Org. Chem.*, 1, 203 (1963); (b) C. A. Coulson and C. W. Haigh, *Tetrahedron*, **19**, 527 (1963).

[34] H. M. McConnell, *J. Mol. Spectrosc.*, **1**, 11 (1957).

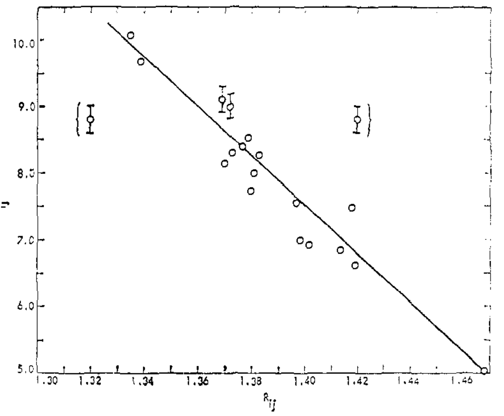

Figure 4. Plot of $^3J$ *vs.* $R_{ij}$ (bond distance). The bracketed values are discussed after footnote *c*, Table II.

Much work[35] has been done on the relation between bond length and $\pi$-bond order, and although this is still not fully rationalized,[36] a general correlation between increasing $\pi$-bond order and decreasing bond length is well established. For those compounds where accurate structural studies have been made, the bond lengths are given in Table I and II, and a plot of $^3J$ *vs.* bond lengths ($R_{ij}$) is given in Figure 4. The correlation exhibits a rather greater linearity over the whole range of bond lengths than does Figure 1, the relationship being

$$^3J = -36.40R_{ij} + 58.46 \tag{4}$$

with $R_{ij}$ in ångströms.

We were interested to see whether this shortening of the C=C bond could account satisfactorily for the observed range of couplings, and also for the observed linear relation between $^3J$ and $R_{ij}$. Karplus[32,37] has discussed the proton–proton coupling in the HC=CH fragment in terms of a valence bond approach, stressing the empirical aspects of the changes produced by variations in the HC=C angles and C=C bond length. It was emphasized that in experimental comparisons with the theoretical results care must be used to isolate the relevant variable, and our attempts to do this by selection of compounds for study have been discussed above.

For an ethylenic system, HC=CH, in which only the C=C distance was allowed to change, Karplus[32] obtained the almost linear dependence of $^3J_{cis}$ with C=C distance, $R_{ij}$, as

$$^3J \cong {}^3J^u\{1 - 2.9(R_{ij} - 1.35)\} \tag{5}$$

where $^3J^u$ is the coupling at the standard ethylenic bond distance, taken here as 1.35 Å. Thus the ratio of the couplings at bond lengths of 1.35 and 1.45 Å can be calculated as 1.41:1. Experimentally the ratio is obtained from Figure 4 as 9.52:5.68 = 1.63:1. Considering the approximations made in the theoretical treatment, for example, the neglect both of any $\pi$-electron contribution and of the influence of the electronic system outside the HC=CH fragment, the agreement is very reasonable.

In view of the recent interest in simple molecular orbital theory,[23,24] we show that conclusions very similar to those of Karplus may be reached using an MO method. We take as our basis the simple molecular orbital theory of hydrocarbons developed by Pople, *et al.*[38,39] This treatment has been criticized[40] for failing to give accurate numerical results unless "wrong" values of valence state ionization potentials are taken for the diagonal matrix elements. However, it is recognized[40] that in spite of these limitations the method can give very satisfactory results when used to correlate coupling constants in a series of similar molecules—presumably because the errors vary fairly smoothly with the coupling constant. For example, the theory has been used[41] to provide a most useful rationalization of the trends in geminal proton–proton couplings.

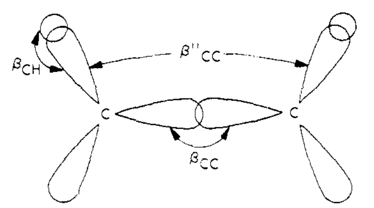

Figure 5. Definition of the overlap integrals ($\beta$'s).

Pople and Santry showed[39] that the expression given by eq 6 could be derived for the *cis* coupling in ethylene.

$$^3J_{cis} \simeq -5Q(\beta_{cis}'')^2/16\beta^3 \tag{6}$$

The $\beta$'s (resonance integrals) are taken[38,39] to be proportioned to overlap integrals and are defined as shown in Figure 5. Since it is found that $\beta_{CC} \approx \beta_{CH}$, $\beta$ is defined as the mean of $\beta_{CC}$ and $\beta_{CH}$. Also

$$Q = \left(\frac{4\pi}{3}g_e\beta_e g_N\beta_N\right)^2[S_H(0)^4]h \tag{7}$$

where $S_H(0)$ is the amplitude of the hydrogen 1s orbital at the proton, $\beta_e$, $\beta_N$ represent the Bohr magneton and nuclear magneton, respectively, and $g_e$ and $g_N$ represent the magnetogyric ratios of electron and nucleus, respectively.

Admittedly, eq 6 only indicates the main effects involved, and the coupling constants will also depend to some extent on parameters ignored in this expression.[40] We stress that we are only making an order of magnitude calculation of the effect of bond length change on the coupling, and for this purpose we make the further assumption that we are dealing with perfect sp$^2$ hybridization, and that altering the C=C distance does not affect the C–H distance, which is taken as 1.06 Å throughout, for consistency with ref 38 and 39. The values of $\beta_{CH}$, $\beta_{CC}$, and $\beta_{CC}''$ are given in terms of the overlaps between carbon 2s, 2p orbitals and hydrogen 1s orbitals by[38]

$$\beta_{CH} = (1/\sqrt{3})\beta_{sh} + (\sqrt{2}/\sqrt{3})\beta_{\sigma h} \tag{8}$$

$$\beta_{CC} = (1/3)\beta_{ss} + (2\sqrt{2}/3)\beta_{\sigma s} - (2/3)\beta_{\sigma\sigma} \tag{9}$$

$$\beta_{CC}'' = (1/3)\beta_{ss} - (\sqrt{2}/3)\beta_{\sigma s} - (1/6)\beta_{\sigma\sigma} + (1/2)\beta_{\pi\pi} \tag{10}$$

where, for example, $\beta_{\sigma h}$ denotes the $\sigma$-type overlap of a

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(35) See ref 20, pp 134–148.

(36) *E.g.*, G. J. Gleicher, *J. Org. Chem.*, 33, 3964 (1968).

(37) M. Karplus, *J. Chem. Phys.*, 30, 11 (1959).

(38) J. A. Pople and D. P. Santry, *Mol. Phys.*, 7, 269 (1964).

(39) J. A. Pople and D. P. Santry, *ibid.*, **9**, 301, 311 (1965).

(40) E. A. G. Armour and A. J. Stone, *Proc. Roy. Soc.* (London), **A302**, 25 (1967).

(41) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, 42, 1339 (1965).

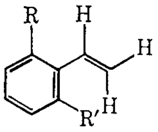
carbon 2p orbital with a hydrogen 1s orbital, and the other definitions follow by analogy. The values of these $\beta$'s may be obtained from the extensive compilation of overlap integrals by Mulliken, *et al.*[42] The Slater exponents taken were 1.0 for H 1s and 1.625 for carbon 2s, 2p orbitals.[37,38] Three $R_{ij}$ values of interest are shown in Table III, together with the values of $(\beta_{CC}'')^2/\beta^3$. Hence at this level of approximation the simple theory suggests that $^3J$ (proportional to $\beta''^2/\beta^3$) should be linear with bond length, within the range of $R_{ij}$ considered, and that the ratio of couplings at $R_{ij}$ = 1.35 and 1.45 Å, respectively, should be approximately 1.25:1, whereas the observed ratio is 1.63:1.

**Table III.** The Variation of the Overlap Integrals ($\beta$'s) with Bond Distance ($R$)

| $R_{ij}$, Å | $\beta_{CC}''$ | $\beta_{CC}$ | $\beta_{CH}$ | $\beta$ | $(\beta_{CC}'')^2/\beta^3$ |
|---|---|---|---|---|---|
| 1.35 | 0.128 | 0.766 | 0.720 | 0.743 | 0.040 |
| 1.40 | 0.119 | 0.746 | 0.720 | 0.733 | 0.036 |
| 1.45 | 0.109 | 0.719 | 0.720 | 0.720 | 0.032 |

## Concluding Remarks

It has been demonstrated that the previously proposed linear relations between $^3J$ and bond order, $p_{ij}$, are no longer followed throughout the whole range of $p_{ij}$ when the accurate values for the coupling constants reported here are used. However, for aromatic systems a new correlation with structure-dependent terms is capable of rationalizing the data to little more than the experimental error (usually ±0.08 Hz). As mentioned above, these effects were previously obscured for several reasons. One of the most severe difficulties is that apparent singlet spectral lines for many aromatic molecules are broad (of the order of 1–2 Hz wide at half-height) and slightly asymmetric in shape even when swept very slowly. The errors in establishing exact transition frequencies result in concomitant uncertainties in the determination of spectral parameters. A striking example of this problem is the spectrum of naphthalene. As shown in Figure 1b, broadening of each apparent singlet arises from extensive inter-ring coupling. Although deuteration at the 1 and 4 positions simplifies the low-field portion drastically, to yield a line width of the order of 0.2 Hz and one-half of a good AA′BB′ spectrum, the upfield signals of this spin system exhibit further long-range, inter-ring couplings which must be over six and seven bonds. The first-order splittings found for these couplings are *ca.* 0.4 and 0.2 Hz. We emphasize that these are tentative values only, given here to provide an estimate of the importance of such couplings in polynuclear aromatics, especially as these have been referred to[7] as "negligible." No information on the signs of these couplings is presently available. Calculations[43,44] of the $\pi$-bond mechanism contribution suggest that this would be positive for the 7 bond and negative for the 6 bond coupling. The significance of the $\pi$-electron mechanism is suggested by the following observation. In the formally similar styrene system



it has been found[45] that the olefinic resonances exhibit long-range (over 6 and 7 bonds) couplings to the aromatic ring, *provided that one or both R, $R^1$ is a proton.* For R, $R^1$ = Me, however, which models show to be incapable of being planar, the olefinic peaks are sharp. This would seem to indicate the necessity for a significant $\pi$ overlap between the aromatic and ethylenic moieties in the transmission of such couplings.

Returning to the values of $^3J$ found in the aromatics, we have suggested that certain of these exhibit the effect of steric interactions. It will be interesting to see whether vicinal couplings between protons in situations which contain even more severe interactions, in, for example, benzophenanthrene, will fit the scheme we propose. It is hoped that the new correlation (eq 3) will serve to stimulate further work, especially in the investigation of the effect of steric interactions on nmr parameters.[46]

**Acknowledgments.** The authors are very grateful to Mr. Haigh (Swansea, England) for helpful discussion and for supplying some of his results prior to publication, and also to Dr. H. Günther (Cologne, Germany), who has informed us that he too has reanalyzed naphthalene and anthracene.

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[42] R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 17, 1248 (1949).

[43] M. Barfield, *ibid.*, 48, 4458, 4463 (1968).

[44] M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, in press, contains a comprehensive survey of experimental data and theoretical treatments.

[45] S. L. Manatt, unpublished work.

[46] Since this work was completed, a paper on the pmr spectrum of 3,4-benzopyrene (**14** in the present work) has appeared (C. W. Haigh and R. B. Mallion, *J. Mol. Spectrosc.*, **29**, 478 (1969)). Our assignment and magnitude of $J_{12}$ in this molecule are in agreement with this work, and these authors also comment on the enhancement of $^3J$ to overcrowded protons. In a private communication, Mr. C. W. Haigh has informed us that he has completed the analyses of some further polycyclic aromatics, including the highly strained benzo[*c*]phenanthrene and dibenzo[*c,g*]phenanthrene. It may be that these new results will require slight modification or extension of the scheme of steric contributions we have proposed here.