The Effect of Steric Compression on Proton–Proton, Spin–Spin Coupling Constants. Further Evidence and Mechanistic Considerations[1]

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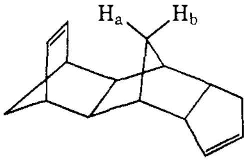
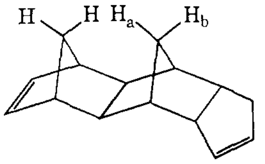
Abstract: Analyses of the nmr spectra of 1,4-dimethylnaphthalene, 1,4-di-*t*-butylnaphthalene, and benzo[*c*]-phenanthrene are presented. These results confirm earlier suggestions that nmr spin–spin coupling constants involving a proton in a sterically compressed situation exhibit appreciably different magnitudes from couplings found in less crowded but otherwise similar environments. A detailed discussion of the mechanisms producing these changes in the case of three-bond, *ortho* couplings ($^3J_{HH}$) is given, and it is shown that the behavior of $^3J_{HH}$ in overcrowded molecules is consistent with the occurrence of strain-relieving distortions in molecular geometry such as have been independently proposed on theoretical grounds. The use of nmr coupling constants as qualitative measures of strain-induced deformations in overcrowded aromatic molecules is discussed.

It has been recognized for some time that nuclear magnetic resonance (nmr) chemical shifts are sensitive to steric interactions between the nucleus in question and nonbonded, but spatially close, groups. The mechanism producing this shift to low field in the compressed atoms has recently been discussed for the cases of ^{1}H and ^{13}C nuclei.[3,4] More recently, we[5] and other workers[6,7] have suggested that not only the shift of the compressed nucleus, but also its spin–spin couplings to other nuclei in the molecule may be significantly modified. Hitherto, the range of examples has been confined to values of two- and three-bond proton–proton couplings ($^2J_{HH}$ and $^3J_{HH}$, respectively). In the former case it was found that the value of J_{ab} in system I is rather different from J_{ab} in II. In these closely similar molecules, it is hardly likely that the molecular structures in the H_aCH_b groups differ except in the direct spatial compression experienced by H_a in II. It was suggested[7] that this compression leads to a closing of the H_aCH_b bond angle, and consequently to a more negative coupling constant.[8]

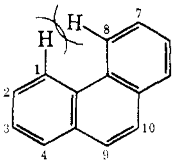


I, J = −10.0 Hz



II, J = −11.0 Hz

To date the evidence for steric enhancement of $^3J_{HH}$ has not been so direct. The effect has so far been noted only in polycyclic aromatic hydrocarbons, for example phenanthrene, III. In this molecule, the values of $^3J_{HH}$ range from J_{23} = 7.00 Hz to J_{9-10} = 9.0 Hz. It is now established[9] that this variation is primarily the result of the linear dependence of $^3J_{HH}$ on the C=C bond length in the *cis*-HC=CH system. However, changes produced by steric compression can be important,[5,6] and a careful distinction between these two effects needs to be made. Thus, having established the form of the relationship between $^3J_{HH}$ and C=C bond length in unstrained systems, we could use it to predict "strain free" values in strained molecules, such as III. In practice, it is more convenient to make use[6,9] of the empirical relation between $^3J_{HH}$ and Hückel π-bond order, p_{ij}, of the C=C bond.[10] This relation has been recently redefined for six-membered aromatic systems as[5]



III

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

In our earlier paper, we found that deviations from eq 1 followed generally consistent patterns which could be rationalized on the basis of steric interactions. For example, where one proton of an *ortho*-coupled pair suffered a steric interaction of the "phenanthric" type (*e.g.*, proton 1 in III), the *ortho* coupling (J_{12} here) exhibited an enhancement of *ca.* 0.3 Hz, relative to the value predicted by eq 1. We have employed the term "steric contributions" for such enhancements of the magnitude of coupling constants. For an interaction of the "naphthalenic" type (*e.g.*, proton 4 in III) an enhancement of *ca.* 0.08 Hz was observed in the *ortho* coupling, in this case J_{34}. For a range of six-membered carbocyclic aromatic molecules containing only interactions of the naphthalenic or phenanthric types, we

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(2) NASA Resident Research Associate, 1968–1970.

(3) B. V. Cheney, *J. Amer. Chem. Soc.*, 90, 5386 (1968).

(4) D. M. Grant and B. V. Cheney, *ibid.*, **89**, 5315 (1967).

(5) M. A. Cooper and S. L. Manatt, *ibid.*, **91**, 6325 (1969).

(6) C. W. Haigh and R. B. Mallion, *J. Mol. Spectrosc.*, **29**, 478 (1969).

(7) R. G. Foster and M. C. McIvor, *Org. Mag. Res.*, **1**, 203 (1969).

(8) See discussion by A. A. Bothner-By, *Advan. Mag. Res.*, **1**, 195 (1965).

(9) For further references and a discussion see ref 5.

(10) This correlation was first discussed by N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962).

showed that our data could be expressed as

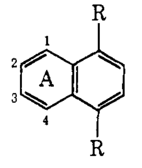
$$^{3}J_{\mathrm{HH}} = 11.60p_{ij} - 0.14 + S_{\mathrm{N}} + S_{\mathrm{Ph}} \qquad (2)$$

where S_{N} and S_{Ph} refer to the enhancement in *ortho*-coupling constant caused by naphthalenic and phenanthric interactions, respectively.

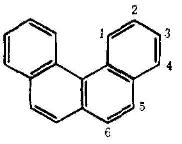
In this paper we have set out to present further evidence for steric contributions to $^{3}J_{\mathrm{HH}}$, and also to discuss the effect of steric compression on $^{4}J_{\mathrm{HH}}$ and $^{5}J_{\mathrm{HH}}$.[11] The factors giving rise to steric contributions will also be detailed. We believe that this discussion will be of general interest, insofar as it suggests comparisons with several theoretical accounts of the deformations in overcrowded aromatic molecules, and also provides a method whereby the magnitude of steric compressional strains may be compared.

Experimental Section

Compounds V (R = D, Me) were obtained commercially, while that with R = *t*-Bu was kindly loaned by Professor R. W. Franck,[12] Fordham University. Benzo[*c*]phenanthrene (VI) was obtained from Professor M. S. Newman, Ohio State University.



Va, R = D
b, R = Me
c, R = *t*-Bu



VI

The spectral analysis of V, R = D has been given previously,[5] and we have discussed the complexity of the spectrum of the parent naphthalene. At the time this work was begun, the only analysis of VI was an approximate, noniterated one.[13] We have since been informed by Haigh,[14] University of Swansea, England, that he has performed accurate analyses of VI and several other polycyclic aromatic compounds.

Spectra were recorded on Varian A-56/60 and HA-100 spectrometers. The concentrations used were approximately 20% (w/v) in $CDCl_3$. Calibration of the spectra was by direct frequency count (HA-100) or the audio side-band method (A-56/60). Transition frequencies used were the mean of at least three spectra, and the rms error of the transition frequencies was 0.03 Hz or less.

The protons of ring A in series V give rise to an AA'BB' spectrum, in which the spectral lines are quite sharp, in contrast to the case where positions 5 and 8 are unsubstituted. In the latter instance,[5] interring couplings to these protons render the lines broad, and the spectra are difficult to analyze accurately. Further details of the spectral analyses are not given here, because of their close similarity to the deuterionaphthalene case, which has been extensively discussed.[5] As before, the spectra were fitted using the program[15] LAOCN3. The chemical shift assignments of V (R = D, *t*-Bu) have been given elsewhere,[5,8] and that for V (R = Me) follows by analogy.

The shift assignment of VI has been discussed by other workers.[13,14] All that was done here was to rerun the spectrum and process the data by use of LAOCN3. The coupling constants are in good agreement with those of Haigh and Mallion.[14]

The results for series V and compound VI are shown in Table I. In Table II are shown values from our previous work[5] on steric contributions to $^{3}J_{\mathrm{HH}}$. The data in Table II are arranged in an order which will be convenient for later discussion.

Table I. Experimental Results[a,b]

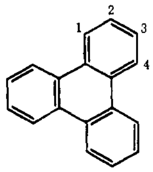
Compd	J_{12}	J_{13}	J_{14}	J_{23}	δ_1	δ_2	RMS
Va	8.30 (0.012)	1.21 (0.010)	0.75 (0.009)	6.86 (0.010)	7.67	7.32	0.028
Vb	8.46 (0.015)	1.34 (0.014)	0.68 (0.012)	6.76 (0.013)	7.91	7.36	0.021
Vc	8.88 (0.016)	1.40 (0.016)	0.63 (0.013)	6.67 (0.015)	8.51	7.42	0.023
	J_{12}	J_{13}	$J_{14}{}^{c}$	J_{23}	J_{24}	$J_{34}{}^{c}$	$J_{56}{}^{c}$
VI	8.62 (0.030)	1.14 (0.030)	0.65 (0.018)	6.88 (0.020)	1.48 (0.026)	7.95 (0.026)	8.62 ±0.05
	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	RMS
	8.98	7.49	7.42	7.79	7.66 7.57		0.050

[a] Chemical shifts in parts per million downfield from TMS in $CDCl_3$ solution; coupling constants given in hertz. Values in parentheses are parameter-set errors. [b] The coupling constants are estimated accurate to ±0.05 Hz. [c] Values calculated from eq 2 are J_{23} = 7.01 Hz, J_{34} = 8.20 Hz, J_{56} = 8.85 Hz.

Discussion

Examination of Table I shows that for series V the effect of successive increases in the size of the group R from D to Me to *t*-Bu is to produce consistent and unambiguous changes in all the proton–proton coupling constants of ring A. An increase in the value of J_{12} with increasing size of the group R is apparent, and would be expected by analogy with the discussions in our previous work.[5] Rather smaller, but nevertheless distinct trends in J_{13} and J_{14} are also found, demonstrating for the first time a steric compression effect on $^{4}J_{\mathrm{HH}}$ and $^{5}J_{\mathrm{HH}}$. The changes in these couplings are much less than those noted in our recent study[11] of the benzocycloalkenes, IV. We emphasize that all the coupling constants for series V exhibit steric effects which may be seen directly, and without the need to use empirical relationships such as eq 1.

A particularly interesting point seen in Table I is that J_{23}, a coupling between two protons neither of which is directly affected by compression, decreases with increased size of the group R in series V. This observation serves to clarify the anomaly which we noted earlier[5] for triphenylene (VII). Whereas a



VII

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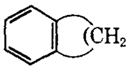
[11] In a recent paper, M. A. Cooper and S. L. Manatt, *J. Amer. Chem. Soc.*, 92, 1605 (1970), we have shown that in benzocycloalkenes, IV, the latter couplings are much more sensitive than $^{3}J_{\mathrm{HH}}$ to molecular distortions.



IV

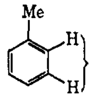
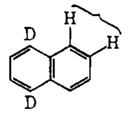
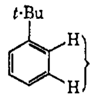
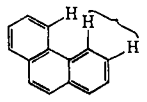
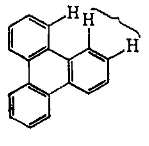
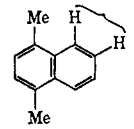
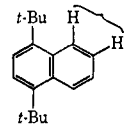
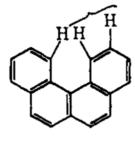
[12] R. W. Franck and K. Yanagi, *J. Org. Chem.*, 33, 811 (1968).

[13] K. D. Bartle and D. W. Jones, *J. Chem. Soc.*, *A*, 437 (1969).

[14] C. W. Haigh and R. B. Mallion, to be published.

[15] An improved version of LAOCOON II: S. M. Catellano and A. A. Bothner-By, *J. Chem. Phys.*, 41, 3863 (1964). We are indebted to Professor Castellano for a listing and description of this program.

Table II. The Magnitudes of Steric Contributions in Some Representative Aromatic Molecules

Compd no.	Molecule[a]	J_{obsd}, Hz	$J_{\text{"strain-free"}}$, Hz	Steric contribution, Hz	Ref
VIII		7.64			*b*
Va		8.30	8.26	0.04	*c,d*
IX		7.96	7.64	0.32	*e,f*
III		8.26	8.00	0.26	*c,d*
VII		8.38	7.78	0.50	*c,d*
Vb		8.46	8.30	0.16	*g,h*
Vc		8.88	8.30	0.58	*g,h*
VI		8.62	8.08	0.54	*d,g*

[a] The coupling considered is between the protons shown bracketed. [b] Values from M. P. Williamson, R. Kostelnik, and S. M. Castellano, *J. Chem. Phys.*, **49**, 2218 (1968). [c] Experimental value from ref 5. [d] Strain-free value estimated from eq 1. [e] Experimental value from S. M. Castellano and R. Kostelnik, *Tetrahedron Lett.*, 5211 (1967). [f] Strain-free value from compound VIII. [g] Experimental value from this work. [h] Strain-free value from compound Va.

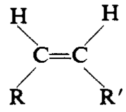
number of other nearly planar aromatic molecules have *ortho*-coupling constants which were well predicted (±0.05 Hz) by eq 2, VII has a value of J_{23} which is *ca.* 0.3 Hz less than that given by this equation.[5] A similar observation[14] has also been made on derivatives of VII. Perhaps the similar behavior of J_{23} in series V and in compound VII and its derivatives is connected with the fact that in these molecules there are two compressions acting on one ring; *i.e.*, both proton 1 and proton 4 suffer compressions. The mechanism producing the decrease in J_{23} is still not completely clear, although we shall see that molecular orbital theory does provide a possible rationalization.

In our earlier work,[5] we suggested that interesting results might be obtained in very highly overcrowded molecules such as benzo[*c*]phenanthrene (VI). From Table I, it is seen that the value of J_{12} in this molecule is indeed larger than predicted by eq 1. This has been the case for all *ortho*-proton–proton couplings so far examined[5,6,14] in aromatic hydrocarbons in which one (or both) of the coupling protons experiences a very severe steric compression.

At the same time, the other *ortho* couplings in VI are all lower than predicted by eq 1 or 2. This may stem from a lack of planarity of VI, which we shall discuss shortly. The Hückel π-bond orders which we have used are calculated[16] assuming planarity of the molecule, and in the case of nonplanar molecules their use provides an even more drastic approximation than is usually the case. Thus, it appears that eq 1 and 2 will have to be applied circumspectly, particularly when strains are large. Nonetheless, for cases where couplings in overcrowded molecules cannot be compared directly with those in otherwise similar, but less crowded molecules (as we have been able to do in series V), the use of empirical methods such as eq 1 to estimate "strain-free" values for couplings is at present the only recourse.

Mechanism of the Steric Effect. It was tentatively suggested[5,6] that in molecules such as phenanthrene (III) the enhancement of J_{12} arose because of the strain relieving splaying apart of the C_1–H_1 and C_8–H_8 bonds. We shall now discuss this hypothesis in more detail, particularly in view of the potential usefulness of steric contributions as a diagnostic tool in the investigation of steric repulsions. Thus we shall consider in turn the various deformations thought to occur in overcrowded molecules and will discuss empirically and also from a molecular orbital viewpoint the effect of these deformations on $^3J_{\text{HH}}$.

It is well known that the value of $^3J_{\text{HH}}$ in the system X may be correlated empirically with several parameters, *viz.*, the electronegativities of the groups R and R′,[17] the HC=C bond angles,[18–21] and the C=C bond distance. The latter correlation[5] is essentially a theoretically more satisfactory reformulation of the older correlation[10] with C=C π-bond order. No extensive work on the dependence of $^3J_{\text{HH}}$ in fragment X with the dihedral angle (φ) between the C–H bonds has been made. This is no doubt because of the lack of suitable compounds for study. It may be tentatively assumed that this dependence would resemble the well-known Karplus $\cos^2 \phi$ relationship[22] found in aliphatic systems.



X

Electronegativity. Evidence has been presented[11] that changes in orbital electronegativities may be important in certain types of angle strain. In the molecules we have studied here, however, the changes in

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(16) "Supplemental Tables of Molecular Orbital Calculations," A. Streitwieser and J. I. Brauman, Ed., with a "Dictionary of π-Electron Calculations," C. A. Coulson and A. Streitwieser, Ed., Pergamon Press, Oxford, 1965.

(17) T. Schaefer and H. M. Hutton, *Can. J. Chem.*, **45**, 3153 (1967).

(18) O. L. Chapman, *J. Amer. Chem. Soc.*, **85**, 2014 (1963).

(19) G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963).

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

(21) M. Karplus, *ibid.*, **85**, 2870 (1963).

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

bond angle and substituents are so slight that this will not be a significant factor.

Distortions in Molecular Geometry. Many workers have discussed the action of molecular distortions in relieving steric strain in overcrowded aromatic molecules.[23–25] Theoretical calculations suggest[24,25] that the most efficient relief of steric strain in these systems is by a series of small deformations throughout the molecule. Unfortunately, it is not easy to check the theoretical treatments against experiment.[24] This arises partly because of the limitations of the X-ray method for structure determination, particularly in regard to proton positions, and partly because of the slight modification of molecular structures occasioned by crystal packing forces relative to the situation in the gas, liquid, or solution phase. For example, out-of-plane bending in triphenylene (VII) occurs to a small but significant extent, as found in the X-ray structure analysis,[26] but theoretical studies suggested[24] that this deformation should be insignificant insofar as intramolecular relief of strain was concerned. It should be realized that in order to evaluate the effect of steric compression on molecular geometry, one needs to estimate the molecular dimensions in the absence of steric effects. This is commonly done[24,25] by using empirical correlations between C=C bond lengths and π-bond orders. For significance to be attached[25] to small differences between observed and calculated C=C bond lengths, this method places a very high degree of reliance in the relationship assumed between bond length and bond order. The problem of estimating "strain-free" geometries by empirical means is somewhat akin to our use of the empirical eq 1 in estimating "strain-free" magnitudes for coupling constants.

Let us consider in detail the distortions thought to occur in phenanthrene (III). Unfortunately, the calculated distortions are very sensitive to the form of the interatomic repulsion force field taken,[24] and so we shall only be able to make an "order-of-magnitude" estimate of the effects produced on $^3J_{HH}$. No one set of authors has considered all the distortions which are of interest to us here, and therefore our account will need to combine two sets of calculations. It is assumed[23,24] that no out-of-plane bending occurs in III. On this basis Gleicher[25] has calculated distortions in bond lengths and bond angles for this molecule. However, he has concentrated on changes in carbon–carbon bond length, and has reported only these. The bond of most interest to us here, *viz.*, C_1–C_2, was predicted to shorten by 2×10^{-3} Å. On the other hand, Coulson and Haigh[24] have calculated C_1–H_1 bond length changes and C=CH bond angle changes in this molecule, but did not consider changes in the C_1–C_2 bond length. Fortunately, the expression used by Gleicher for the van der Waals' repulsive interaction between protons is identical with one used by the other workers, even though the latter did not actually present all the C–H bond length and bond angle changes for this potential. By close examination of Coulson and Haigh's calculations, it is possible to obtain by interpolation the required changes in bond length and bond angle with sufficient accuracy for our purposes. In this way the reduction in the C_1–H_1 distance is found to be 4×10^{-3} Å, and the decrease in the $C_2C_1H_1$ bond angle is found as 1.60°. We now consider the effect of these distortions on $^3J_{HH}$.

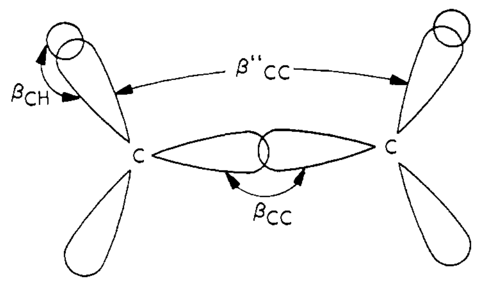

Figure 1. Definition of the overlap integrals (β's).

a. C=C Bond Length. We have proposed[5] for six-membered rings the following relation between $^3J_{HH}$ and the C=C bond length in the *cis*-HC=CH system

$$^3J_{HH} = -36.40R_{ij} + 58.46 \qquad (3)$$

where R_{ij} is the C=C bond distance in ångströms. Hence, the decrease of 2×10^{-3} Å calculated for the C_1–C_2 bond length[24] in phenanthrene would lead to an increase of approximately 0.07 Hz in J_{12}.

b. C=CH Bond Angle. The influence of this parameter on $^3J_{HH}$ in the *cis*-HC=CH fragment has been mentioned in our earlier paper, and so will only be outlined here.[5] In cyclohexene and cyclopentene we have measured couplings of 10.11 and 5.57 Hz, respectively, for values[27,28] of the angle θ of 118.4 and 124.2°. If we assume a linear correlation between $^3J_{HH}$ and θ in this angle range, then a reduction of 1° in both HC=C angles would increase $^3J_{HH}$ by 0.78 Hz. This estimate may only be valid for vicinal protons in an ethylenic system, *i.e.*, at a C=C distance of *ca.* 1.335 Å. For the purposes of this discussion, it will be assumed that the bond angle dependence of $^3J_{HH}$ is independent of the C=C bond distance. In phenanthrene, III, there is a reduction in the angle $C_2C_1H_1$, but not in $C_1C_2H_2$, so that the 1.6° decrease calculated[24] in the former angle would increase J_{12} by 0.62 Hz.

c. CH Bond Length. This is a much harder dependence to evaluate, since we cannot, as above, make use of empirical methods. We shall approach this problem in a manner similar to that used previously[5] to provide a theoretical rationale of eq 3.

Using a simple, semiempirical molecular orbital theory, People and Santry[29] derived the following approximate expression for the *cis* coupling in ethylene

$$^3J_{cis} \simeq k(\beta''_{cis})^2/(\beta_{CH} + \beta_{CC})^3 \qquad (4)$$

where k is a constant and the β's (resonance integrals) are taken as being proportional to overlap integrals and are defined as in Figure 1. The mathematical expressions for the β's are given elsewhere.[5,29] For our purpose it is enough to say that we may assume

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(23) For a review see G. Ferguson and J. M. Robertson, *Advan. Phys. Org. Chem.*, **1**, 203 (1963).

(24) C. A. Coulson and C. W. Haigh, *Tetrahedron*, **19**, 527 (1963).

(25) G. J. Gleicher, *J. Org. Chem.*, **33**, 3964 (1968).

(26) F. R. Ahmed and J. Trotter, *Acta. Crystallogr.*, **16**, 503 (1963).

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

(28) G. W. Rathjens, *ibid.*, **36**, 2401 (1962).

(29) J. A. Pople and D. P. Santry, *Mol. Phys.*, **9**, 301, 311 (1965).

that when the C–H bond length is reduced, only the magnitude of β_{CH} will be affected, and this may be calculated from the tables of Mulliken.[30] For compatibility with earlier work,[5,29] we take the unperturbed C–H distance as 1.060 Å. In phenanthrene (III), the decrease in the C_1–H_1 distance is calculated[24] to be 4×10^{-3} Å, hence we take this distance as 1.056 Å. The respective values of β_{CH} are 0.720 and 0.722. Hence we can see that this would slightly reduce the coupling $^3J_{HH}$, rather than increase it. Inserting numerical values[5] into eq 3, it is found that this C–H bond length reduction, if both C–H bonds are affected, and if $^3J_{HH} \approx 8$ Hz, would reduce $^3J_{HH}$ by some 0.03 Hz. When only one bond length is affected, as in III, a reduction of 0.015 Hz may be estimated. This change is negligible by comparison with the other effects considered above. However, it must be remembered that this is only an "order-of-magnitude" calculation.

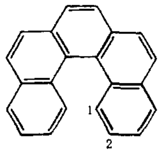
The net effect of these three geometrical distortions, *a*, *b*, and *c*, is therefore calculated to be an increase of 0.67 Hz, which is larger than the observed value in phenanthrene (0.26 Hz) by a factor of ~3. Nonetheless, in view of the nature of the approximations involved, and the present state of theoretical understanding of vicinal proton–proton couplings, the agreement is sufficiently good to suggest that the major steric contribution to this coupling arises from in-plane bending. This is in line[23] with the much lower energies of bond-angle bending processes as opposed to bond-length changes. As we have discussed earlier, the experimental X-ray data are insufficiently accurate to enable these theoretical results to be confirmed. The moderately good agreement we have obtained between the observed and calculated effects on $^3J_{HH}$ suggests a way of testing the theoretical work, and may hold promise for future studies of strain induced molecular distortions.

We turn now to consider triphenylene (VII). The steric contribution to J_{12} is found experimentally to be 0.50 Hz, as opposed to 0.26 in phenanthrene (III). Available theoretical calculations[24,25] of distortions for these two molecules use the same potential functions and are qualitatively similar, with the decrease in $C_2C_1H_1$ being rather larger for VII (1.74°) than for III (1.60°). The greater value of the steric contribution to J_{12} in VII over that in III is then rationalized at least in a qualitative manner.

While the increase in J_{12} in VII may be at least qualitatively explained, we note that no changes in the bond lengths or bond angles in the $H_2C_2C_3H_3$ moiety are found, and so the decrease in J_{23} (0.30 Hz in VII) is difficult to explain on this basis. In triphenylene no out-of-plane bending has been predicted,[24] except with the use of very "hard" and unlikely potential functions for interatomic repulsion. Hence, loss of planarity would not seem to be a plausible explanation for the behavior of J_{23} in VII, but there are molecules where this deformation is significant. We now go on to discuss this situation.

Out-of-Plane Bending. In certain very highly strained molecules, *e.g.*, benzo[*c*]phenanthrene (VI), out-of-plane bending is known to be present to a large extent. Thus the X-ray analysis[31] of this molecule shows a dihedral angle in the $H_1C_1C_2H_2$ system of 13°. Using the Karplus $\cos^2 \phi$ relation, a coupling $^3J_{HH}$ of *ca.* 8 Hz for a planar system would be reduced by 0.4 Hz as a result of this distortion. The observed enhancement[15] in J_{12} of 0.44 Hz shows that this reduction must be outweighed, presumably by in-plane bond angle deformations such as we have discussed above for III and VI.

Again in pentahelicene (XI), there is severe buckling which creates nonplanarity in the $H_1C_1C_2H_2$ fragment.



XI

Nonetheless, an enhancement[14] of J_{12} is again observed (8.51 Hz as compared to a calculated value of 8.07 Hz using eq 1). Theoretical calculations of the deformations in both VI and XI have been made.[32,33] These disregard any in-plane bending of the H–C bonds, and stress the role of out-of-plane bending. While the latter mechanism is undoubtedly of prime importance, the nmr results strongly suggest that there is nonetheless appreciable in-plane bending, and this will need to be considered in any more accurate calculations on these molecules.

In dealing with nonplanar molecules such as VI and XI, the $\cos^2 \phi$ dependence of $^3J_{HH}$ would be expected to reduce the magnitudes of these couplings below the values in a planar system. It is not surprising therefore that eq 1 and eq 2 would predict values which are too high, unless there is a compensating positive steric contribution caused by direct steric compression, as for J_{12} in these molecules. As we have noted earlier, the Hückel π-bond orders are calculated assuming planarity of the carbon skeleton, and therefore eq 1 and eq 2 must be used with caution in dealing with nonplanar molecules.

Molecular Orbital Treatment. We have now considered the range of geometrical distortions thought to occur in overcrowded molecules.[24] There still remains the possibility that the "sterically induced charge polarization of the H–C bond," proposed by Cheney[3] to account for the chemical shifts of compressed protons, might *per se* affect the magnitudes of the coupling constants. This possibility is not approachable by empirical methods, and we have attempted to treat this problem with the aid of coupling constants calculated using extended Hückel molecular orbital theory (EHT),[34] and also the CNDO/2 treatment[35] of Pople and Segal. These methods undoubtedly have limitations,[36] so that our calculations may have only heuristic value, but in a number of cases[11,37,38] the trends cal-

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

(31) F. L. Hirschfeld, S. Sandler, and G. M. J. Schmidt, *J. Chem. Soc.*, 2108 (1963).

(32) F. L. Hirschfeld, *J. Chem. Soc.*, 2126 (1963).

(33) C. A. Coulson and S. Senent, *ibid.*, 1819 (1955).

(34) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(35) J. A. Pople and G. A. Segal, *ibid.*, **43**, S139 (1965).

(36) M. J. S. Dewar, in "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967.

(37) R. C. Fahey, G. C. Graham, and R. L. Piccioni, *J. Amer. Chem. Soc.*, **88**, 193 (1966).

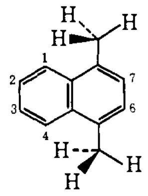
(38) D. T. Clark, *Tetrahedron*, **24**, 2663 (1968).

culated by EHT or CNDO/2 reproduce satisfactorily the experimental behavior.[39]

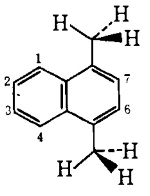
Values of the input parameters for EHT were as used in previous work.[11] In all cases the standard bond length C═C (aromatic) = 1.40 Å, C–C (aliphatic) = 1.54 Å, and C–H = 1.10 Å were taken. All sp^3 carbons were assigned tetrahedral symmetry, and all bond angles to sp^2 carbon were taken as 120°, except where stated. The *ortho*-proton–proton coupling constants were calculated from the expressions for the Fermi contact term given by Pople and Santry.[11,40] Two sets of calculations were performed. In the first set, no geometrical distortions were allowed in an attempt to discover whether steric repulsion *per se* could produce the observed changes in coupling constants through a "charge polarization" [3] mechanism. Thus values of $^3J_{HH}$ in XII and the even more strained XIII were compared (Table III). Second, the compressed protons 1 and 4 of XIII were given small in-plane displacements. A typical value of θ = 1° in XIV was taken. Table III shows that the results are in poor agreement with both the observed steric contributions and our empirical treatment of the in-plane distortion, so that the significance of these values must not be pursued too far. It may be seen, however, that EHT and CNDO/2 theories disagree on the effect of increasing compression in the absence of distortion. The former calculates a decrease in J_{12} and increase in J_{23} on-going from XII to XIII while the latter theory calculates the complete opposite. Interestingly, both calculate that in-plane distortion of bond angle (XIII to XIV) would increase J_{12} and decrease J_{23}. Thus the behavior of the latter coupling in triphenylene (VII) and in series V may possibly arise concomitantly with the increase in J_{12} as a result solely of the in-plane motion of H_1 and H_4. It is not possible to arrive at a definite conclusion on the importance of "charge polarization" mechanisms because of the conflicting theoretical results. It is likely that CNDO/2, which unlike EHT includes electron repulsions, is[41] the more valid treatment under the present circumstances. Therefore, we cannot rule out the intervention of this mechanism. The problem awaits improved theoretical treatments, and so does our proposal that a decrease in J_{23} automatically accompanies an increase in J_{12} in molecules such as XIV.

Table III. Calculated Coupling Constants

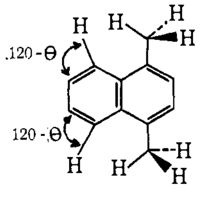
Molecule	EHT J_{12}	EHT J_{23}	CNDO/2 J_{12}	CNDO/2 J_{23}
XII	3.697	3.862	3.512	3.779
XIII	3.641	3.875	3.529	3.765
XIV	3.670	3.846	3.560	3.745



XII



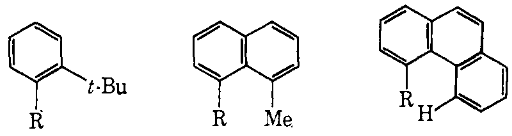
XIII



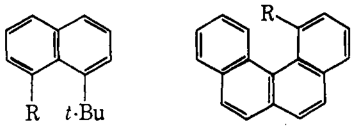
XIV

Steric Contributions to $^3J_{HH}$ as Measures of Steric Strain. In our earlier work[5] we assumed that the enhanced magnitudes of coupling constants involving protons in overcrowded situations could be adequately defined by eq 2 and we obtained, as discussed, generally satisfactory results. Nonetheless, even at that time, there were certain anomalies. For example, the value of J_{23} in triphenylene (VII) was difficult to explain, because the steric overcrowding here is at first sight very similar to that in phenanthrene (III). We now discuss this point in some detail, and widen our account to a more general discussion of the applicability of nmr coupling constants to the estimation of steric strains.

We take as our starting point a suggestion[42a] made by Newman, and foreshadowed rather earlier[42b] by Brown and coworkers. These workers have proposed that substituent groups which are chemically distinct may, by reason of their similar steric sizes, give rise to similar compressions. For example, it was suggested[42a] that the steric strains experienced by the substituent R in the environments of the type A would be very similar. By extension, the more severe strains existing at R in the environments labeled B would again be expected to be similar. Now for each of these different environments, A and B, we have available values for the *ortho* coupling constants, J_{HR}, when R is a proton. For similar magnitudes of strain at R, we should expect to obtain similar steric contributions to J_{HR}, which may serve as a test of the above picture of the equivalence of strains.



A



B

Table II shows the steric contributions to $^3J_{HH}$ for a number of molecules with compressional effects analogous to those in environments A and B. For the molecules IX, III, VII, and Vb, which are examples of environment A, the steric contributions to J_{12} range from 0.16 Hz to 0.50 Hz. For Vc and VI, which are examples of the still more strained environment B, the steric contributions of 0.58 and 0.54 Hz are nearly equal. Note that we should not necessarily expect the steric contributions in B to be larger than A, because it is possible that out-of-plane bending[31] of

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[39] This is particularly so for the case of $^3J_{HH}$: M. A. Cooper and S. L. Manatt, *Org. Mag. Res.*, in press, and unpublished work.

[40] J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

[41] We are grateful to a referee for emphasizing this and other points relative to our discussion.

[42] (a) M. S. Newman and W. H. Powell, *J. Org. Chem.*, **26**, 812 (1961); (b) H. C. Brown, G. K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson, and K. L. Nelson, *J. Amer. Chem. Soc.*, **75**, 1 (1953).

the group R may also contribute to the value of J_{12} in the former case.

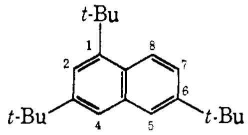
At first sight, it may seem that the spread found for the steric contributions in environment A is disproof of the equivalent strain model. We suggest that this scatter arises in a very subtle way. Even in the most similar geometries, *e.g.*, III and VII, there are slight differences in C=C bond lengths which mean that the distances from substituent R to the nearest proton of the crowding group will in general not be exactly equal.[24] The nonbonded interactions between these groups will be of the van der Waals type, and therefore will be critically dependent on this distance. Thus even in very similar cases there will usually be slightly different steric strains requiring rather different amounts of strain-induced deformation of the group R. The success of the equivalent strain concept[42] suggests that the strains in, for example, the environment we have designated A will be equal within *ca.* 1 kcal/mol. An energy expenditure of only 1 kcal/mol is, however, sufficient to deform a C=CH bond angle by approximately 5°. This corresponds to a change in $^3J_{HH}$ of *ca.* 2 Hz. In view of the sensitivity of $^3J_{HH}$ to slight bond angle distortions, it is hardly surprising that the steric contributions to coupling constants in series A, *viz.*, 0.3 ± 0.2 Hz do not give *exact* agreement. Nevertheless, the use of steric contributions to $^3J_{HH}$ seems to provide a sensitive method for investigating small molecular deformations and suggests that for series A the distortion of the C=CH angle is in each case close to 1°

Concluding Remarks

Further and less ambiguous evidence for the effect of steric compression on proton–proton nmr coupling constants has been given above. It has been shown that these effects are satisfactorily explained on the basis of strain-relieving in-plane bending. However, in highly strained molecules such as VI and XI, the effect of this bending on $^3J_{HH}$ may be partially offset by out-of-plane bending. The observed steric contributions support theoretical treatments of the distortions in overcrowded molecules.

Although it seems possible to use nmr coupling constants as probes into molecular deformations in at least a qualitative manner, perhaps the technique of nuclear Overhauser enhancement[12,43] will provide more information on interproton distances than will the use of coupling constants.

Steric contributions may find useful diagnostic application in structural determinations. For example, we have examined[44] the pmr spectrum of 1,3,6-tri-*t*-butylnaphthalene (XII). Its proton spectrum has one low-field proton, well separated from the other aromatic protons, which is a broad doublet exhibiting a 9.2-Hz coupling. On chemical shift grounds, this may tentatively be assigned to H_8 because of the severe deshielding effect of the *peri-t*-butyl group. Nonetheless, the coupling constant itself is capable of yielding useful information. In an unsubstituted naphthalene J_{78} is 8.30 Hz as we have discussed. The influence of a *peri-t*-butyl group increases this value to 8.88 Hz. Furthermore, we have seen that in *t*-butyl benzene J_{23} is 7.96 Hz as opposed to 7.56 Hz in benzene itself. If the steric contributions to $^3J_{HH}$ are additive, therefore, we may estimate that J_{78} in XII would be increased *ca.* 0.4 Hz by the substitution of *t*-Bu for H at position 6. We then finally estimate J_{78} in XII as *ca.* 9.28 Hz. This value is in good agreement with the observed value of 9.2 Hz and helps confirm the proposed structure for XII that was based principally on the mode of synthesis.



Acknowledgments. We are very grateful to Professors R. W. Franck and M. S. Newman for supplying samples, and to Professor Franck and Mr. C. W. Haigh for helpful discussion and communication of results prior to publication.[45]

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(43) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5250 (1965).

(44) Work in cooperation with Professor R. W. Franck; R. W. Franck, to be published.

(45) NOTE ADDED IN PROOF. Since completion of this work, an analysis of the nmr spectrum of 1,5-dimethylnaphthalene (XV) has appeared [K. D. Bartle and D. W. Jones, *J. Mol. Spectrosc.*, **22**, 353 (1969)]. The coupling constants obtained by this noniterative procedure were: J_{23} = 6.9 Hz, J_{24} = 0.9 Hz, and J_{34} = 8.9 Hz. The latter value in particular is in poor agreement with our value of 8.46 Hz for J_{12} in Vb, although steric interactions in the two molecules should be similar. We have therefore rerun the spectrum of XV using an iterative ABC analysis on the methyl-decoupled system. We obtain [M. A. Cooper and S. L. Manatt, unpublished work] J_{23} = 6.93 Hz, J_{24} = 1.14 Hz, and J_{34} = 8,52 Hz. These latter values are in much better agreement with our data for Vb, and serve to emphasize that because steric contributions are small (*ca.* 0.5 Hz), great care is needed in the analysis of spectra, otherwise experimental error may obscure these subtle effects.