^3J(HH)—$P_{\mu,\nu}$ Correlation for Planar 7-Membered Cyclic π-Systems—Structural Effects on ^3J(HH)†

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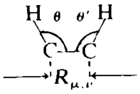
It is shown that sterically unperturbed vicinal HH coupling constants in planar 7-membered π-systems correlate linearly with the HMO π-bond order: $^3J(\mathrm{HH}) = 20.91P_{\mu,\nu} - 3.85$ (r.m.s. error 0.26 Hz, correlation coefficient =0.988). Systematic deviations from this relationship which most probably originate from valence angle changes are found for fused π-systems containing rings of different size. Model calculations using the CNDO/2 method as well as finite perturbation theory and INDO wave functions support the experimental findings. An improvement of existing ^3J(HH)—$P_{\mu,\nu}$ correlations for planar 6-membered rings is possible if CNDO/2 π-bond orders are used instead of HMO or PPP-SCF data.

INTRODUCTION

Following theoretical calculations[1] and experimental results,[2] vicinal HH coupling constants in planar unsaturated hydrocarbons are found to depend on the CC bond length $R_{\mu,\nu}$ and the HCC valence angles θ and θ'. Detailed structural information for new compounds can thus be obtained in a relatively straightforward manner through the analysis of the ^{1}H n.m.r. spectrum if ^3J(HH)—$R_{\mu,\nu}$ or ^3J(HH)-bond angle correlations are known with sufficient accuracy.



From these correlations the ^3J(HH)—$R_{\mu,\nu}$ relationship has been studied most extensively for unsaturated 6-membered rings.[3,4] Results for 5-membered rings have recently been presented.[5] In addition, linear correlations between ^3J(HH) and the MO π-bond order $P_{\mu,\nu}$, first formulated for benzenoid hydrocarbons in 1962,[6] are available for 5-[7] and 6-membered rings.[3,4]

Similar studies for unsaturated 7-membered rings did not progress beyond a first limited attempt.[8] Since we recently determined the ^3J(HH) data for the benztropylium ion (**1**),[9] we felt that a closer inspection of a ^3J(HH)—$P_{\mu,\nu}$ relationship for 7-membered rings would be rewarding. In order to obtain additional experimental data the ^{1}H n.m.r. spectra of dicyclopenta[*ef*, *kl*]heptalene (**2**) and its dihydro derivative (**3**) (Fig. 1) were analysed.[10]

RESULTS AND DISCUSSION

The spectra of **2** and **3** have been reproduced elsewhere;[11] **2** yields an AX_2 system ($\delta_A = 7.24$, $\delta_X = 8.55$ ppm, $J(AX) = 9.63$ Hz) for the protons of the 7-membered ring and an additional singlet ($\delta = 8.25$ ppm) for those of the 5-membered ring. $J(12) = 4.5$ Hz was thus determined from the ^{13}C satellites. The one bond ^{13}C, ^{1}H coupling constants, also obtained from the ^{13}C n.m.r. spectrum of **2**, showed a remarkable dependency on ring size. For the 5-membered ring 167 Hz was found, whereas for the 7-membered ring values of $^1J(C_AH) = 156$ and $^1J(C_XH) = 151$ Hz were observed. For **3**, in addition to two singlets at δ 2.21 (CH_2 protons) and δ 6.69 (five ring protons) an AMX system was observed and analysed ($\delta_A = 6.34$, $\delta_M = 4.92$, $\delta_X = 5.58$ ppm, $J(AM) = 10.46$, $J(MX) = 8.46$, $J(AX) = 1.35$ Hz). The assignment of the proton resonance frequencies of **3** was based on the finding $J(AM) > J(MX)$. This relationship follows from the CC bond length of $R_{AM} = 0.1368$ nm and $R_{MX} = 0.1424$ nm, determined for the closely related 3,5,8,10-tetramethylaceheptylene,[12,13] and the inverse ^3J(HH)—$R_{\mu,\nu}$ proportionality[1]. It is further supported by the π-bond order relationship derived below. The ^3J(HH) data for **1–3** are given in Table 1 together with vicinal coupling constants from the literature for a number of structurally related systems[14–20] which are collected in Fig. 1. For the following discusion we assume that the 7-membered rings in **1–8** are virtually planar, a realistic hypothesis in view of the available X-ray data.[12,13,21]

Since to our knowledge CC bond length data have been determined for only a few of these systems (**6**[21], **10**[22]), we used HMO π-bond orders for the elucidation of a ^3J(HH) correlation with structural features in the 7-membered rings of **1–11**. As Fig. 2 demonstrates, a good linear relationship is obtained. Using only data from **1**(*a*, *b*), **2**(*a*), **3**(*b*), **4**(*b*), **7**(*a*, *b*), and **8**(*a*, *b*)—a limitation that will be justified below—yields

$$^3J(\mathrm{HH}) = (20.91 \pm 1.25)P_{\mu,\nu}(\mathrm{HMO}) - (3.85 \pm 0.79) \quad (1)$$

with a correlation coefficient $R = 0.988$ and a standard deviation of 0.29 Hz. The data for **9**, **10**, and **11** have

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† Proton Magnetic Resonance Spectra of Unsaturated Ring Systems, Part XXIV; for Part XXIII see Ref. 47.

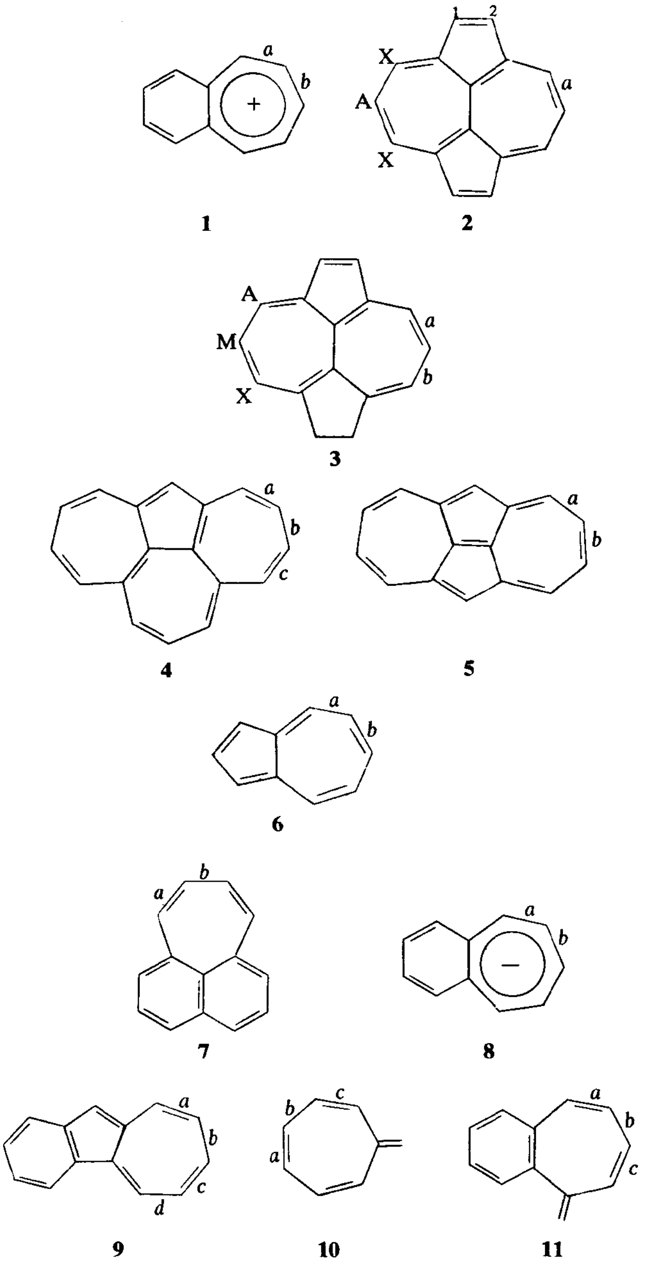


Figure 1. Planar cyclic π-systems containing 7-membered rings.

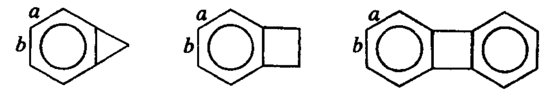
been excluded from the regression analysis because of their lower accuracy (estimated error ±0.2 Hz[8,19,20]) and the possibility that **11** is not fully planar.[23] Despite this restriction these coupling constants fit the general slope nicely. On the other hand, a number of points obviously deviate from relationship (1) in a systematic manner and they were also excluded from the calculation.

A closer inspection of the above mentioned deviations reveals that they are due to coupling constants of HC⋯CH fragments in the neighbourhood of annelated 5-membered rings. As an example we mention azulene (**6**) where coupling in *a* is found too low and coupling in *b* too high. Similar observations are made for couplings in fragments *a* of **3** and **4** and, most pronounced, for both couplings *a* and *b* of **5**. As is well known from investigations dealing with 6-membered rings[4,24] and cyclic olefins,[25] strain effects may introduce changes in HCC bond angles, thereby causing changes in vicinal HH coupling.[1] It is therefore interesting to remember that fusion of a smaller ring to a 6-membered ring also decreases the coupling in fragment *a* and increases that in fragment *b*, as is exemplified if the data for benzocyclopropene (**12**),[24] benzocyclobutene (**13**),[4] and biphenylene (**14**)[24] are compared with the benzene value (7.54 Hz[26]):

Table 1. Vicinal H,H coupling constants in HC⋯CH fragments of planar 7-membered rings in bi- and polycyclic π-systems

Compound	HC⋯CH-fragment	$P_{\mu,\nu}$ (HMO)	^3J(HH)	Ref.
1	*a*	0.674	10.34	9
	b	0.629	9.52	9
2	*a*	0.656	9.63	this work
3	*a*	0.719	10.46	this work
	b	0.568	8.46	this work
4	*a*	0.740	10.74	14
	b	0.547	7.66	
	c	0.738	12.26	
5	*a*	0.707	9.91	15
	b	0.590	10.23	
6	*a*	0.664	9.5	16
	b	0.639	10.3	
7	*a*	0.763	12.23	17
	b	0.527	6.73	
8	*a*	0.726	11.06	18
	b	0.575	8.19	
9	*a*	0.698	10.9	8
	b	0.604	8.5	
	c	0.673	10.9	
	d	0.621	8.2	
10[a]	*a*	0.738	10.8	19
	b	0.536	8.0	
	c	0.765	12.0	
11	*a*	0.770	11.5	20
	b	0.521	6.8	
	c	0.772	11.5	

[a] Coupling constants are those for the 8,8′-dicyano compound.



	12	13	14
J(Hz) *a*	6.04	7.36	6.89 (7.03)
b	7.63	7.78	8.23 (7.91)

For **14** these changes are also a result of strong variations in the CC π-bond orders, but even after correction for this effect using the relationship

$$^3J = 12.47P_{\mu,\nu}(\mathrm{HMO}) - 0.71 \qquad (2)$$

derived for unstrained aromatic systems,[4] a substantial difference between predicted values (in parentheses) and observed ones remains.

On the other hand, fusion of a larger ring to a smaller one causes changes of opposite sign for the ^3J(HH) values in the latter. A notable example is found with the benzocyclooctatetraene dianion (**15**).[9,27] In this and similar cases, in addition to possible strain effects, van der Waals effects will be most probably responsible for the observed trends, as is suggested by the findings for *o*-di-*t*-butylbenzene

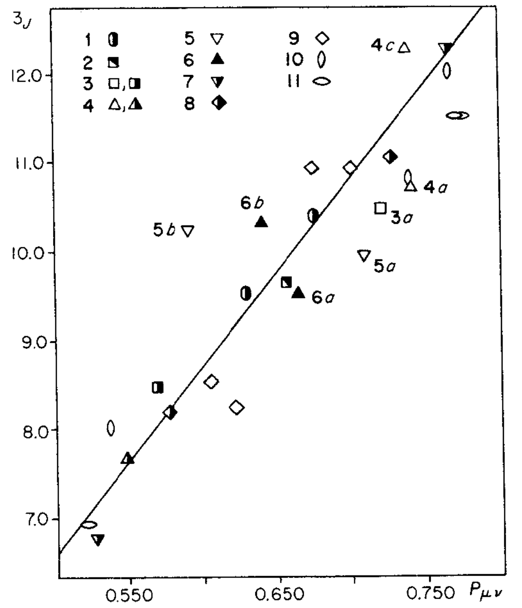
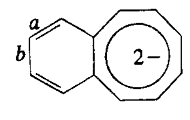
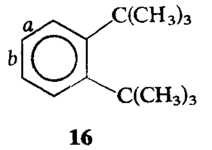


Figure 2. ^3J(HH)—$P_{\mu,\nu}$(HMO) correlation for systems **1–11**; points used for the least squares fit of Eqn (1) are marked by half filled symbols.

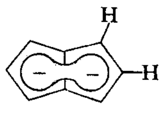


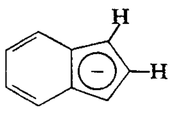


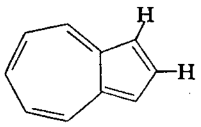
	15	**16**
J(Hz)	a 8.51	8.11
	b 5.80	7.00

(**16**)[28] and several benzenoid aromatics like phenanthrene[3,4] or 3,4-benzpyrene.[29]

Additional data which support the above mentioned observations comes from the series pentalene dianion (**17**),[30] indenyl anion (**18**),[9] and azulene (**6**),[16] where the coupling increases despite constant π-bond order:



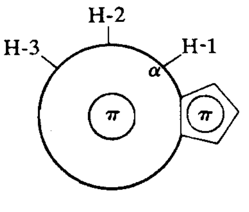




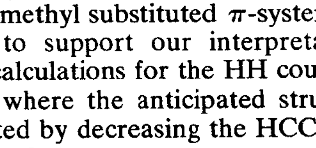
	17	**18**	**6**
$P_{\mu,\nu}$(HMO)	0.650	0.659	0.656
J(HH)[Hz]	3.0	3.4	4.0

We therefore conclude that deviations from linear ^3J(HH)—$P_{\mu,\nu}$ correlations are to be expected in bi- and polycyclic π-systems if fused rings of different size N are present. In particular, two distinct situations may be anticipated:

Type A. Fusion of a small ring ($N<6$) to a larger one causes $J(12)$ to decrease and $J(23)$ to increase:

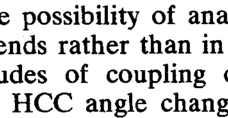


Type B. Fusion of a larger ring to a smaller one causes $J(12')$ to increase and $J(2'3')$ to decrease:



Clearly, these rules only describe the general trend that most probably originates mainly from HCC bond angle changes as a result of steric strain or compression. They can hardly be formulated quantitatively and the ultimate magnitude of the ^3J(HH) changes is determined by the individual structural situation and can only be assessed where complete structural data are available. In particular less pronounced changes or violations of the rules formulated above are to be expected in cases where the fused rings differ by only one carbon unit. For example, the ^3J(HH) values in the 6-membered ring of indane[3] show small changes of opposite sign to that expected for a type A arrangement. Similarily, in the indenyl anion both vicinal coupling constants in the 6-membered ring (8.05, 6.51 Hz[9]) are reduced if compared with values expected on the basis of the HMO π-bond order[4] (8.15, 6.75 Hz). Furthermore, fusion of two planar rings with more than six carbon atoms will always lead to steric compression of the type observed for **15**, as is exemplified by the deviation of coupling c in **4**. Nevertheless, especially for the smaller rings up to the 7-membered rings, a general picture for the rationalization of observed trends for HH coupling constants in fused polycyclic π-systems seems to emerge from this study that may also be helpful to understand the structural dependency of vicinal ^{13}C, ^{1}H coupling constants in methyl substituted π-systems.[31]

In order to support our interpretation we have carried out calculations for the HH coupling constants in benzene, where the anticipated structural changes were simulated by decreasing the HCC valence angles θ at C-1 and C-4:



The results, obtained for $\theta = 120°$, 118°, 116° and 114° on the basis of the Pople–Santry theory[32] within the CNDO/2 approximation[33] and, in addition, with the finite perturbation method[34] using INDO wave functions[33] are summarized in Table 2.

As in other cases, the usefulness of such approaches lies mainly in the possibility of analysing experimentally observed trends rather than in the calculation of absolute magnitudes of coupling constants. It thus appears that the HCC angle changes introduced are appropriate to induce the ^3J(HH) changes of type A and type B discussed above, since we find that $J(12)$ decreases and $J(23)$ increases, whereas the opposite is true for $J(12')$ and $J(2'3')$, respectively. The type A perturbation therefore seems to increase the HCC

Table 2. Calculated HH coupling constants for distorted benzene (in Hz) and 2s, 2s-bond orders $P_{1s,1s}$($\times -10^4$)

CNDO/2	$\theta = 120°$	118°	116°	114°
$J(12)$	5.24	5.16	5.08	5.01
$J(23)$	5.24	5.30	5.36	5.41
$J(12')$	5.24	5.32	5.40	5.48
$J(2'3')$	5.24	5.17	5.10	5.02
$J(13')$	1.08	1.05	1.02	0.99
$J(13)$	1.08	1.11	1.15	1.18
$J(14)$	0.39	0.39	0.39	0.39
$P_{1s,1s}(1,2)$	944	938	931	924
$P_{1s,1s}(2,3)$	944	949	954	958
$P_{1s,1s}(1,2')$	944	950	955	960
$P_{1s,1s}(2',3')$	944	939	933	926
FP-INDO				
$J(12)$	8.54	8.40	8.29	8.17
$J(23)$	8.54	8.63	8.76	8.82
$J(12')$	8.54	8.67	8.83	9.02
$J(2'3')$	8.54	8.41	8.30	8.15

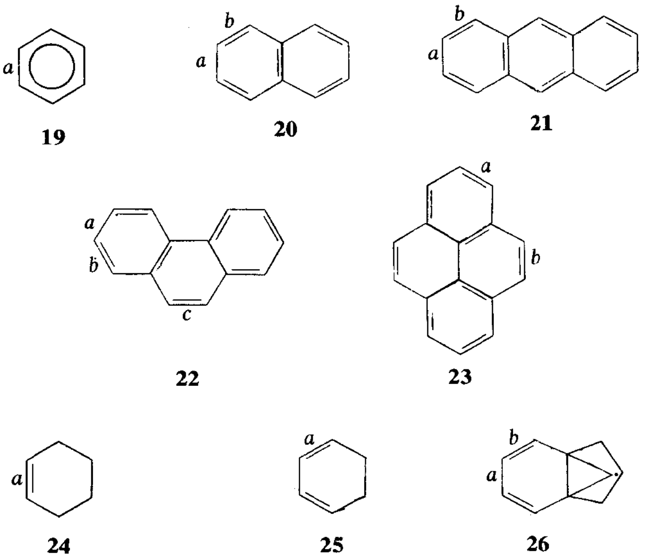


Figure 3. Aromatic and olefinic cyclic π-systems containing 6-membered rings.

valence angle in the α-position, a fact simulated within our model by the proton sequence H-1, H-2, H-3, H-4, whereas the type B perturbation—simulated by the proton sequence H-1, H-2′, H-3′, H-4—decreases this angle. It is noteworthy that the change of only one pair of valence angles is sufficient to introduce the changes for all the vicinal coupling constants in an alternating manner. As an inspection of the CNDO/2 density matrix shows, these changes are a result of parallel changes of the 1s–1s bond orders between the protons under consideration. The CCπ-bond order, on the other hand, is completely unaffected by the structural alteration.

Cooper and Manatt, in their analysis of strain effects on HH coupling constants in 6-membered rings[24] only found small and unsystematic trends for the vicinal parameters. The reason for this might be seen in the inclusion of planar α,α'-diketones, where electronic effects may mask the steric influences.

As for the long range coupling constants ^4J and ^5J, we calculate changes (Table 2) that are different from those observed in strained bicyclic systems like **12** and **13**.[3,4,24] Since earlier calculations[35] using the same theoretical model, however with minimized geometries, reproduced the experimental trends correctly, it must be concluded that bond length and CCC-angle changes are of considerable importance for ^4J and ^5J values also.

Possible improvements of ^3J(HH)—$P_{\mu,\nu}$ correlations

Despite the progress made in theoretical calculations of spin–spin coupling,[39] empirical correlations between H,H coupling constants and structural or theoretical parameters are still useful since they allow—within a more limited set of compounds—rather precise predictions. In an earlier paper we demonstrated that different ^3J(HH)—$P_{\mu,\nu}$ correlations exist for aromatic and olefinic π-systems in cases of 6-membered rings if HMO or PPP-SCF-$P_{\mu,\nu}$ data are used. It was suggested that this is a consequence of the shortcomings within both π-electron theories and that an advanced theoretical treatment would be more successful.

Using now a set of sterically unperturbed ^3J(HH) data in 6-membered rings of compounds **19–26** (Fig. 3 and Table 3) and CNDO/2 calculations for the 2p$_z$-CC-bond orders in these systems we derive from a linear regression analysis

$$^3J(\mathrm{HH}) = (9.60 \pm 0.18)P_{\mu,\nu}(\mathrm{CNDO/2}) + (1.25 \pm 0.13) \quad (3)$$

with a standard deviation of only 0.08 Hz and a correlation coefficient of 0.998.

EXPERIMENTAL

Degassed samples of **2** and **3** (0.2 M in CS_2 with *c.* 10% tetramethylsilane added as internal reference)

Table 3. Vicinal H,H coupling constants in sterically unperturbed HC═CH fragments of planar 6-membered rings

Compound	HC═CH-Fragment	$P_{\mu,\nu}$(CNDO/2)	^3J(HH) calculated	^3J(HH) experimental	Ref.
19	*a*	0.667	7.66	7.54	26
20	*a*	0.736	8.32	8.28	4
	b	0.589	6.91	6.85	4
21	*a*	0.756	8.51	8.55	4
	b	0.563	6.66	6.59	4
22	*a*	0.614	7.15	7.20	36
	b	0.714	8.11	8.11	36
	c	0.795	8.89	9.00	3
23	*a*	0.669	7.68	7.72	3
	b	0.799	8.92	8.80	3
24	*a*	0.904	9.93	10.00	4
25[a]	*a*	0.859	9.50	9.46	4
26	*a*	0.830	9.22	9.25	37
	b	0.477	5.83	5.94	37

[a] Because of the torsion around the C-2—C-3 bond in cyclohexa-1,3-diene[38] only the coupling constant across the double bond was considered.

were measured with a Varian HA 100 spectrometer using side band calibration. The experimental error in line position was 0.05–0.09 Hz. ^{13}C satellites were determined with a CAT computer using 50 transients at a sweep width of 5 Hz cm.$^{-1}$ ^{13}C n.m.r. spectra were recorded with a Bruker HX-90 spectrometer at 22.63 MHz using the FT mode. These results have been cited elsewhere.[11]

The HMO calculations were performed with the program of Heilbronner and Straub.[42] For the CNDO/2 and INDO calculations[43] standard geometry and parameters[33] were used with the following exception: the CNDO/2 program was modified for the use of one centre repulsion integrals as given by Sichel and Whitehead[44] and the calculation of two centre repulsion integrals by the Ohno procedure.[45] It was shown earlier[46] that this modification improves the calculated H,H coupling constants.

CONCLUSION

The results of this work yield a guideline for the interpretation of vicinal HH coupling constants in fused ring systems, and add to the available ^{3}J(HH)—$P_{\mu,\nu}$ (HMO) correlations for 5-[7] and 6-membered rings[3,4] those for 7-membered rings. In cases where points from 'aromatic' compounds (bond order range 0.4 to 0.8) and 'olefinic' compounds (bond orders <0.4 or >0.8) fall on different correlation lines, better results are obtained if CNDO/2 π-bond orders are used, a possibility that has not yet been tested for 5- or 7-membered rings.

Equation (1) may be useful for studies concerned with the electronic structure of cyclic π-systems, where arguments based on chemical shifts often fail to allow conclusive answers, in particular in cases of charged species or compounds that contain groups with large diamagnetic anisotropies (–CN, –C≡C–). As pointed out elsewhere,[40,41] ^{3}J(HH) values on neighbouring HC—CH fragments are therefore sensitive probes of electronic structure, especially if methods to account for other influences, like valence or torsional angle changes, are available.†

Acknowledgement

We are indebted to Professor Dr C. Jutz, Munich, for kindly providing us with samples of **2** and **3** and to cand. chem. H. von Puttkamer for his assistance in the HMO calculations. Financial support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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† As this work was completed, we received information[31a] that Braun and Kinkeldei derived a ^{3}J(HH)—$R_{\mu,\nu}$ correlation for planar 7-membered rings using selected values of experimental and calculated CC bond lengths and corrections for HCC valence angles (S. Braun and J. Kinkeldei, *Tetrahedron*, in press).

REFERENCES

1. M. Karplus, *J. Am. Chem. Soc.* **85**, 2870 (1963).
2. For a summary see H. Günther, *NMR-Spektroskopie*, G. Thieme Verlag, Stuttgart (1973).
3. M. A. Cooper and S. L. Manatt, *J. Am. Chem. Soc.* **91**, 6325 (1969).
4. H. Günther and J. B. Pawliczek, *Tetrahedron* **26**, 1755 (1970).
5. H. L. Ammon and G. L. Wheeler, *J. Am. Chem. Soc.* **97**, 2326 (1975).
6. N. Jonathan, S. Gordon and B. P. Dailey, *J. Chem. Phys.* **36**, 2443 (1962).
7. W. B. Smith, W. H. Watson and S. Chiranjeevi, *J. Am. Chem. Soc.* **89**, 1438 (1967).
8. D. J. Bertelli and P. Crews, *Tetrahedron* **26**, 4717 (1970).
9. H. Günther, A. Shyoukh, D. Cremer and K. H. Frisch, *Liebigs Ann. Chem.* in press.
10. For the synthesis of **2** and **3** see C. Jutz and E. Schweiger, *Synthesis* 193 (1974).
11. H. Günther and H. Schmickler, *Pure Appl. Chem.* **44**, 807 (1975); see also Ref. 10.
12. E. Carstensen-Oeser and G. Habermehl, *Angew. Chem.* **80**, 564 (1968).
13. R. Quasba, F. Brandl, W. Hoppe and R. Huber, *Acta Crystallogr.* **B25**, 1198 (1969).
14. D. E. Jung, *Tetrahedron* **25**, 129 (1969).
15. K. Müllen and H. Reel, *Helv. Chim. Acta* **56**, 363 (1973).
16. D. Meuche, B. B. Molloy, D. H. Reid and E. Heilbronner, *Helv. Chim. Acta* **46**, 2483 (1963).
17. D. Wendisch, W. Hartmann and H.-G. Heine, *Tetrahedron* **30**, 295 (1974).
18. S. W. Staley, private communication.
19. The data given are those of the 8,8'-dicyano derivative: D. J. Bertelli, T. G. Andrews Jr and P. O. Crews, *J. Am. Chem. Soc.* **91**, 5286 (1969).
20. D. J. Bertelli, J. T. Gerig and J. M. Heberlin, *J. Am. Chem. Soc.* **90**, 107 (1968).
21. G. S. Pawley, *Acta Crystallogr.* **18**, 560 (1965).
22. For data on the 8,8'-dicyano derivative see H. Shimanouchi, T. Ashida, Y. Sasada, M. Kakudo, I. Murata and Y. Kitahara, *Bull. Chem. Soc. Jpn* **39**, 2322 (1966).
23. D. J. Bertelli, *Topics in Nonbenzenoid Aromatic Chemistry*, p. 29. J. Wiley & Sons, New York (1973).
24. M. A. Cooper and S. L. Manatt, *J. Am. Chem. Soc.* **92**, 1605 (1970).
25. M. A. Cooper and S. L. Manatt, *Org. Magn. Reson.* **2**, 511 (1970).
26. J. M. Read Jr, R. E. Mayo and J. H. Goldstein, *J. Mol. Spectrosc.* **22**, 419 (1967).
27. H. Günther, A. Shyoukh, D. Cremer and K. H. Frisch, *Tetrahedron Lett.* 781 (1974).
28. S. M. Castellano and R. Kostelnik, *Tetrahedron Lett.* 5211 (1967).
29. C. W. Haigh and R. B. Mallion, *J. Mol. Spectrosc.* **29**, 478 (1969).
30. T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.* **85**, 2030 (1963).
31. (a) S. Braun, personal communication; (b) U. Vögeli and W. v. Philipsborn, *Org. Magn. Reson.* **7**, 617 (1975).
32. J. A. Pople and D. P. Santry, *Mol. Phys.* **8**, 1 (1964).
33. J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw Hill, New York (1970).
34. J. A. Pople, J. W. McIver Jr and N. S. Ostlund, *J. Chem Phys.* **49**, 2960, 2965 (1968).
35. C. S. Cheung, M. A. Cooper and S. L. Manatt, *Tetrahedron* **27**, 701 (1971).
36. R. C. Fahey and G. C. Graham, *J. Phys. Chem.* **69**, 4417 (1965).
37. H. Günther and H.-H. Hinrichs, *Liebigs Ann. Chem.* 706, 1 (1967).
38. H. Oberhammer and S. H. Bauer, *J. Am. Chem. Soc.* **91**, 10 (1969).
39. P. D. Ellis and R. Ditchfield, *Topics in Carbon-13 NMR-Spectroscopy*, Vol. 2, p. 434. Wiley-Interscience, New York (1976).

40. H. Günther and R. Wenzl, *Z. Naturforsch. Teil B* **22**, 389 (1967).
41. H. Günther, *Tetrahedron Lett.* 2967 (1967).
42. E. Heilbronner and P. A. Straub, *Hückel Molecular Orbitals,* Springer Verlag, Berlin (1966).
43. QCPE program No. 91 and 281.
44. J. M. Sichel and M. A. Whitehead, *Theor. Chim. Acta* **11**, 263 (1968) and earlier papers by these authors.
45. K. Ohno, *Theor. Chim. Acta* **2**, 219 (1964).
46. D. Cremer, Ph. D. Thesis, University of Cologne (1972).
47. H. Günther, J.-B. Pawliczek, J. Ulmen and W. Grimme, *Chem. Ber.* **108**, 3141 (1975).

Received 30 March 1977; accepted 15 April 1977