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CALCULATIONS OF GEOMETRIES OF ORGANIC MOLECULES USING THE CNDO/2 MOLECULAR ORBITAL METHOD—II

STRUCTURAL PREDICTIONS FOR THE BENZOCYCLOALKENES, AND A THEORETICAL RATIONALIZATION OF THEIR PROTON-PROTON SPIN-SPIN COUPLING CONSTANTS*

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Abstract—The CNDO/2 semiempirical MO method is applied to calculations of the geometries of some strained benzocycloalkenes. The strain-induced bond length distortions predicted are in disagreement with earlier work, although the lack of accurate experimental data precludes a decision as to the validity of either treatment. The CNDO/2 wavefunctions are examined for features which may throw light on previous qualitative descriptions which have been proposed to account for recent experimental data on this series, such as NMR and ESR spectra, and rates of electrophilic substitution. In particular, trends in the proton-proton spin-spin coupling constants in the benzocycloalkenes and also benzene, naphthalene and biphenylene are well accounted for by the CNDO/2 wavefunctions.

In PART I,[1] we noted how the lack of experimental data on molecular geometries had in certain cases hampered the detailed interpretation of some NMR results we have recently obtained. Calculations on strained cycloalkenes and on some typical aromatic molecules were undertaken using the semi-empirical CNDO/2 treatment of Pople *et al.*[2,3] It was found that CNDO/2 calculated and experimental C—C bond lengths ($\mathbf{R}_c$ and $\mathbf{R}_o$, respectively) could be correlated to a high degree of accuracy using the equation

$$\mathbf{R}_o = \mathbf{R}_c + 0.001263\, n_H/(1.563 - \mathbf{R}_c) \qquad (1)$$

where n_H is the number of H atoms attached to the C—C bond. Eq (1) was obtained in Part I from a consideration of the systematic differences between observed and CNDO/2 calculated bond lengths in a range of small unstrained acyclic molecules. The further generally good agreement obtained from Eq (1) for cycloalkenes and three polycyclic conjugated molecules (naphthalene, biphenylene and azulene) encouraged us to hope that meaningful calculations of molecular geometries might still be obtained when the cycloalkene fragment is fused with an aromatic system as in the benzocycloalkenes.

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Details of the general procedure of calculation have been given before,[1] and need not be repeated here, except to note that the C—H distances were taken from analogous calculations in Part I and were not varied in the energy minimizations. Furthermore, these C—H bonds were taken to bisect the exterior C–C–C angles at the relevant C-atoms. Neither of these approximations is expected to introduce significant errors into the calculated geometries, particularly insofar as the carbon skeleton is concerned. In each case a planar geometry for the carbon skeleton was imposed. For benzocyclopentene (indane), and particularly for benzocyclohexene (tetralin), the assumption of planarity will give rise to excess strain in the alicyclic ring, but the effect of this on the geometry of the aromatic moiety would be expected to be minimal (*vide infra*).

DISCUSSION

The CNDO/2 calculated molecular geometries for the benzocycloalkenes are given in Table 1. Values in parentheses have been processed by Eq (1). It is interesting to compare these results with those for a hypothetical strain-free *ortho*-dialkyl benzene. Although no experimental data are available for such a molecule, we may assume that the bond lengths would be close to those found in benzene itself (1·397 Å experimentally). The results obtained for tetralin by energy minimization are all close to this value. This confirms that strain effects are unimportant in the tetralin molecule insofar as the geometry of the benzene ring is concerned. This is in accord with chemical experience.[4]

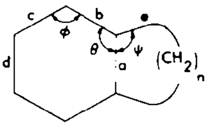


FIG 1

Examination of the theoretical results in Table 1 shows that the effect of fusing increasingly strained rings on the benzene nucleus, from tetralin to benzocyclopropene leaves bond *d* (Fig 1) essentially unchanged, increases bond *c* slightly (*ca* 0·016 Å), increases bond *a* by *ca* 0·020 Å, and decreases bond length *b* by *ca* 0·025 Å. It is important to assess the extent to which these predicted bond length changes may be relied upon. First, we note the excellent agreement between CNDO/2 calculated and experimental bond lengths found for the polycyclic aromatic systems, e.g., naphthalene, in Part I. On the other hand, for example, the value of bond length *a* in benzocyclopropene (1·420 Å) may be an overestimate by *ca* 0·025 Å [*cf* the values found for cyclopropene in Part I, which are (Experimental) 1·300 Å, and (Eq (1)) 1·325 Å]. Turning to benzocyclobutene, we again calculate that bond length *a* is significantly longer than in a strain free system. The bonds analogous to *a* in biphenylene and cyclobutene are quite well calculated by CNDO/2 and are within 0·006 Å of the experimental values, whether or not Eq (1) is used. On this basis, therefore, it can be argued that the predicted increase of bond length *a* in benzocyclobutene does arise because of the strain and is not wholly a result of cumulative errors in the calculations. Similar arguments may be advanced for indane. Nonetheless, it is perhaps wise to place more confidence in the *direction* of bond length changes predicted than on the *magnitudes* of the changes. With this reservation, we now compare the present work with previous investigations of the molecular geometries of the benzocycloalkenes.

No highly accurate experimental structural data on the benzocycloalkenes is available, although X-ray crystallographic studies have been made on dichlorobenzocyclobutene[5] and the even more highly strained [1,2:4,5]benzodicyclobutene.[6] CNDO/2 calculations on the latter molecule are also given in Table 1. In neither of these studies, at their present levels of refinement, were the bond lengths obtained felt to be accurate to better than 0·02 Å, or to be significantly different from the bond length in benzene. In the case of bond angles, however, both studies found that fusion of the strained alicyclic moiety led to an increase in angle θ (Fig 1) and a decrease in angle ϕ. For the benzocyclobutene, these angles were measured[6] as 123° and 114°, respectively, while for the benzodicyclobutene θ was reported to be 126° and ϕ as 108°. In each case CNDO/2 somewhat underestimates these angle changes.

The only previous theoretical study on the geometries of benzocycloalkenes of which we are aware was made some 25 years ago for the case of indane.[7] The latter workers predicted that the strain caused by fusion of the alicyclic moiety would give rise to bond angle changes in the benzene ring, in agreement with the present CNDO/2 results and the X-ray data. However, it was also concluded that the bond length changes resulting would primarily be a decrease in bond length *a* (Fig 1) and an increase in bond length *d*. This result is in disagreement with the CNDO/2 study, and the conflict may best be resolved by accurate experimental structural data. We hope that the present work will stimulate interest in this area.

There are other features resulting from our calculations on the benzocycloalkenes which are of interest relative to recent work in this area. Studies have been made on the NMR spectra,[4] electron paramagnetic resonance spectra (of radical anions),[8] polarographic reduction potentials,[9] and rates of electrophilic substitution[10] and metalation[11] of the benzocycloalkenes and related molecules. The following model has been proposed[10] as a qualitative account of the electronic structure of these compounds. In a structure such as Fig. 2, it has been stated that, "the atomic orbitals of the fused aryl carbon used to construct the strained ring have higher *p*-character. Hence, the remaining orbital has higher *s*-character. The ortho-carbon (i.e. C_1) is thus bound to an orbital of higher electronegativity." This was held to account for the observation[10] that "aryl positions adjacent to a fused strained ring have enhanced acidity and reduced reactivity towards electrophilic substitution."

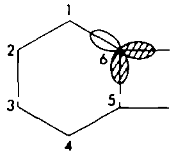


FIG 2. Shaded orbitals have increased *p*-character, hence unshaded orbital has higher *s*-character.

In Table 2 we list the C_{2s} and $C_{2p\pi}$ bond orders for the aromatic rings in the benzocycloalkenes. These bond orders show qualitatively the same behavior, namely that strain reduces these bond orders in bonds C_1—C_2 and C_5—C_6, and increases the bond orders in C_2—C_3 and C_1—C_6 (Fig 2). This is in line with the suggestions made by Streitwieser.[10] The C_{2s} and $C_{2p\pi}$ orbital charges on each atom are given in Table 3 together with the total atomic charges on carbon. The effect of increased strain, going from tetralin to benzocyclopropene, is to increase the total electron density at C_6, while the $2p\pi$ electron density decreases markedly and there is no consistent behavior in the $2s$ electron density. For C_1 the total electron density decreases with strain, as does the $2s$ electron density, while the $2p\pi$ density decreases from tetralin to benzocyclobutene and then increases again in benzocyclopropene. For C_2 there is a slight increase in total electron density, occasioned by almost cancelling changes in the $2s$ and $2p\pi$ electron densities. It is therefore not an easy matter to find consistent trends in all these electron densities from which to discuss Streitwieser's "orbital electronegativity" proposals.[10]

We have examined the CNDO/2 wavefunctions for features which might account for the observations first that in the radical anions of the benzocycloalkenes, ring strain increases the hyperfine splitting constant for the proton on C_1, but decreases that with the proton on C_2,[8] and second that the polarographic reduction potentials[9] of the benzocycloalkenes are reduced by strain. Results of simple Hückel π-electron calculations which allow increased electronegativity at C_1 and decreased electronegativity at C_2 account for both these observations.[8,9] No smooth behavior in either case is predicted by CNDO/2. However, the observed trends in proton–proton spin–spin coupling constants for the benzocycloalkenes are well reproduced by CNDO/2 as we shall now discuss.

NMR EVIDENCE

We have discussed elsewhere[4,12–15] the sensitivity of vicinal proton–proton spin–spin coupling constants ($^3J_{HH}$) to structural features in carbocyclic molecules. In our study[4] of the NMR parameters of benzocycloalkenes, it was found that values of $^3J_{HH}$ were insensitive to strain, with the exception of J_{12} in benzocyclopropene, which was significantly smaller than the other values. At the same time, $^4J_{HH}$ (i.e. J meta) decreased sharply, and $^5J_{HH}$ (J para) increased sharply with strain. It proved possible to rationalize the latter trends on an empirical basis with the assumption that partial bond-fixation was occurring.[7,16] Originally, we assumed[4] that strain caused structure **A** to contribute more to the hybrid than structure **B** (Fig 3).

A **B**

FIG 3

However, our present work casts doubt on this explanation and suggests that **B** actually becomes the dominant structure in the lower benzocycloalkenes. Note that the empirical evidence adduced for partial bond-fixation from the behavior of $^4J_{HH}$ and $^5J_{HH}$ is not affected by the theoretical work. It is the occurrence of bond-fixation in any sense, i.e. either **A** or **B** becoming dominant as opposed to a fully delocalized π-electron system as in benzene, that provides the rationale in empirical terms. In regard to $^3J_{HH}$, it was tentatively suggested[4] that the indecisive behavior of this coupling constant arises out of a cancellation of bond length and bond angle factors which would be present in A, but not in B. Lack of structural data means that this proposal has to await substantiation, although extended Hückel MO theory calculations[4] on model systems without invoking bond length changes went some way towards suggesting that the bond angle changes might be important. The present work has provided a set of theoretical geometries for the strained benzocycloalkenes. Using these CNDO/2 geometries and the corresponding eigenvectors and eigenfunctions, it is possible to perform an approximate calculation of the magnitudes of the proton–proton nmr coupling constants using the formula of Pople,[4,17]

$$J_{AB} = (64/9)\,\beta^2\gamma_A\gamma_B h(S_A\,|\delta(r_A)|\,S_A)(S_B\,|\delta(r_B)|\,S_B) \times \sum_{i}^{\text{occ}}\sum_{j}^{\text{unocc}} (\varepsilon_i - \varepsilon_j)^{-1} C_{is_A}C_{js_A}C_{js_B}C_{is_B} \qquad (2)$$

where the symbols have their usual meanings.[4,17] Three points about the use of this formula must be noted. First, we are calculating only the σ-electron contribution to the coupling and ignoring any coupling mechanism via the π-electrons. This approximation is expected to be reasonable[18] for the case of $^3J_{HH}$, but is doubtful[19] in the case of $^4J_{HH}$ and $^5J_{HH}$. Second, the absolute magnitudes of the present calculated coupling constants are not so important as the trends predicted along a similarly constituted set of compounds,[4,20,21] which are often in good agreement with experiment, especially for $^3J_{HH}$. In view of this we have used Eq. (2) as it stands rather than the more complicated form of this equation[17] more properly used with self-consistent field MO-theories. Our previous calculations have shown[14] that for a fixed carbon skeleton, the calculated values of J are altered by less than 0·05 Hz for a change in C–C–H angle of 1°. Thus our initial assumption that C—H bonds will bisect C–C–C angles will not affect the calculations as to coupling constants.

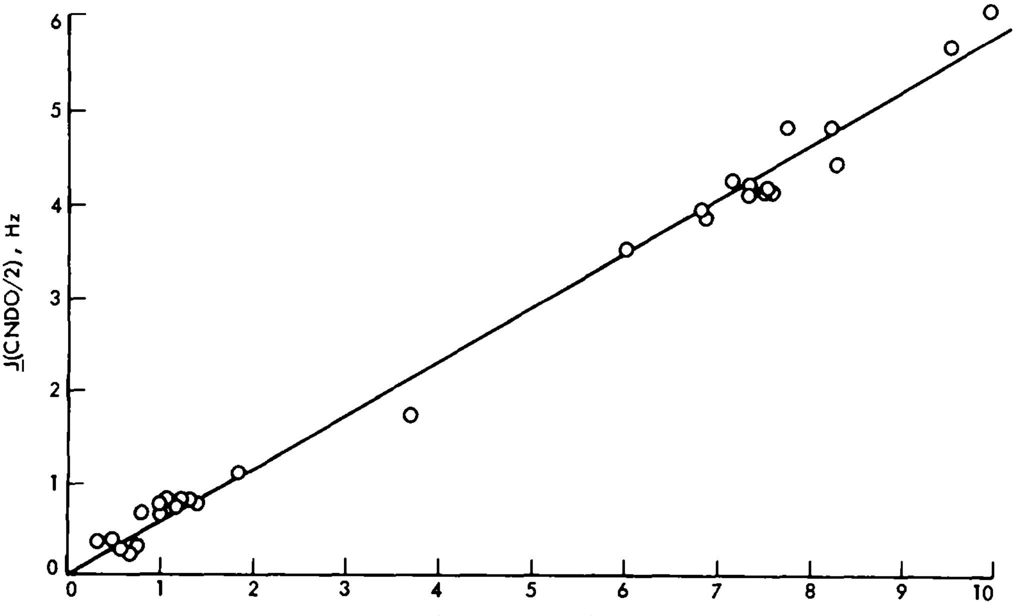


FIG 4. Observed and calculated proton–proton spin–spin coupling constants for aromatic molecules

Table 4 and Fig 4 compare the observed and calculated values of $^3J_{HH}$, $^4J_{HH}$ and $^5J_{HH}$ for the aromatic rings of the benzocycloalkenes together with benzene, naphthalene, biphenylene and azulene. All the calculations of coupling constants have been made on the CNDO/2 minimized molecular geometries of Part I. Lack of data for the benzocycloalkenes would in any case preclude calculations based on experimental geometries. Also, calculations, based on model systems, e.g. using a regular hexagon for the benzene moiety in benzocycloalkenes, give trends in poor agreement with experiment.[4,21] Calculations using a geometry with uniform C—C bond lengths in the aromatic system but allowing changes in bond angles also give considerable scatter in the predicted trends.

From our results, it is possible to establish a good correlation between observed and calculated coupling constants by the simple equation:

$$J_{\text{observed}} = 1{\cdot}700\, J_{\text{CNDO/2}} \tag{3}$$

The equation is followed with an rms deviation of less than $\pm 0{\cdot}3$ Hz in a range of *ca* 10 Hz. We have noted above that the significance of this agreement must be treated with reserve for $^4J_{HH}$ and $^5J_{HH}$. However, it is interesting that CNDO/2 faithfully reproduces the very small value of $^4J_{HH}$, and very large value of $^5J_{HH}$ found in benzocyclopropene. These values, which are found experimentally to be 0·33 Hz and 1·85 Hz, respectively, are to our knowledge the limiting lower and upper values found for these coupling constants in benzene derivatives. In this connection it is interesting that CNDO/2 predicts that $^5J_{HH}$ in [1,2:4,5] benzodicyclobutene would be even larger than the value in benzocyclopropene (CNDO/2 values calculated to be 1·35 Hz and 1·15 Hz, respectively).

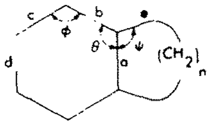
Turning to the values of *ortho* coupling constants, it is seen that the large values (*ca* 10 Hz experimentally) in the 7-membered ring of azulene, and the much smaller values (*ca* 3·7 Hz experimentally) in the 5-membered ring of azulene are well reproduced by Eq (1). For the coupling constants in 6-membered rings, it is pleasing that CNDO/2 reproduces the small value of J_{12} found in benzocyclopropene. Considering solely the benzocycloalkenes, the experimental value of 6·04 Hz in benzocyclopropene is the only *ortho*-coupling constant which is more than *ca* 0·2 Hz different from the mean value of *ca* 7·5 Hz. Similarly, the CNDO/2 calculations predict a value of 3·51 Hz for this coupling in benzocyclopropene, while the values of J_{12} for rest of the benzocycloalkenes are close to 4·2 Hz.

The good agreement between the trends in coupling constants predicted by CNDO/2 and found experimentally has also been noted within other series of closely related molecules. For example, the couplings found in benzene, pyridine and pyridinium cation have been rationalized on this basis,[20] as have the values in tropene, tropolone and azulene.[22]

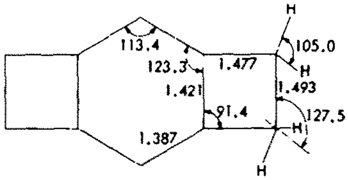
CONCLUSION

Based on our examination of the theoretical and experimental results presented here and in the previous paper, it seems that CNDO/2, used with caution, may be useful for interpretation of subtle electronic structural effects such as proton–proton coupling constants. In the present work, use of CNDO/2 has led to good agreement for the geometries of benzene, naphthalene, azulene and biphenylene, as well as for the trends in coupling constants found in these molecules. Thus it is tempting to speculate that the good agreement between observed and calculated trends in coupling constants for the benzocycloalkenes may mean that the CNDO/2 predicted geometries are significantly close to the real geometries. It is hoped that our results will prompt future careful experimental structure determinations on this series of molecules. This should provide the ultimate test of the geometries calculated by the CNDO/2 method.

TABLE 1. CNDO/2 CALCULATED GEOMETRIES OF BENZOCYCLOALKENES AND BENZODICYCLOBUTENE



	Aromatic nucleus[a,b]						Alicyclic ring[a,c]	
n	a	b	c	d	θ	φ	e	ψ
1	1·420	1·365	1·400	1·382	122·6	114·8	1·458	60·8
	(1·420)	(1·372)	(1·416)	(1·396)			(1·482)	
2	1·421	1·379	1·391	1·381	121·4	116·5	1·476	91·5
	(1·421)	(1·386)	(1·406)	(1·395)			1·505	
3	1·412	1·389	1·386	1·384	119·8	119·8	1·472	109·7
	(1·412)	(1·396)	(1·400)	(1·398)			(1·500)	
4	1·403	1·392	1·383	1·383	118·7	122·0	1·470	121·4
	(1·403)	(1·399)	(1·397)	(1·397)			(1·498)	
	1·397	1·397	1·397	1·397				



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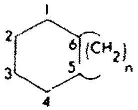
[a] Bond lengths in Å, bond angle in degrees. Values in parentheses are from Eq (1).

[b] C—H bonds given same length as in CNDO/2 result for benzene (1·117 Å) and taken to bisect C–C–C angles.

[c] C—H bonds given same length as in CNDO/2 calculations on cycloalkenes (Part I) and taken to bisect C–C–C angles.

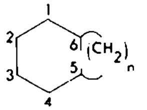
[d] Values for a hypothetical strain-free *o*-dialkylbenzene (see text).

TABLE 2. CNDO/2, C_{2s} AND $C_{2p\pi}$ BOND ORDERS FOR AROMATIC RINGS OF BENZOCYCLOALKENES



	Bond orders							
	C_{2s}				$C_{2p\pi}$			
n	1-2	2-3	1-6	5-6	1-2	2-3	1-6	5-6
1	0·3389	0·3572	0·3846	0·2345	0·6089	0·7147	0·7119	0·5695
2	0·3392	0·3487	0·3506	0·2387	0·6374	0·6892	0·6864	0·5902
3	0·3411	0·3431	0·3361	0·2942	0·6615	0·6671	0·6613	0·6165
4	0·3413	0·3390	0·3307	0·3186	0·6741	0·6551	0·6483	0·6302
Benzene	0·3412	0·3412	0·3412	0·3412	0·6667	0·6667	0·6667	0·6667

TABLE 3. CNDO/2, C_{2s} AND $C_{2p\pi}$ ORBITAL CHARGES AND TOTAL ATOMIC CHARGES ON CARBON IN BENZOCYCLOALKENES

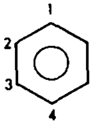
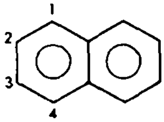
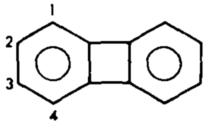
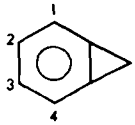
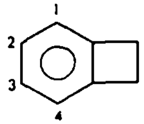
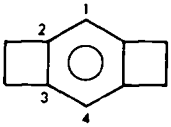
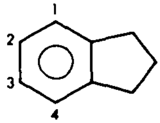
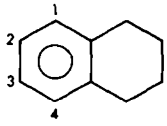
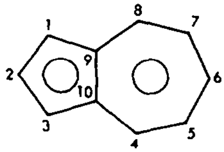


	Charges in electrons								
	C_{2s}			$C_{2p\pi}$			Total atomic charge		
n	C_1	C_2	C_6	C_1	C_2	C_6	C_1	C_2	C_6
1	1·0006	1·0138	0·9754	1·0225	1·0063	0·9503	3·976	3·993	4·016
2	1·0109	1·0084	0·9775	1·0080	1·0047	0·9916	3·997	3·989	3·991
3	1·0115	1·0080	0·9864	1·0116	1·0019	0·9976	4·000	3·989	3·987
4	1·0128	1·0076	0·9757	1·0141	0·9988	1·0010	4·000	3·989	3·986
Benzene	1·0083	1·0083	1·0083	1·0000	1·0000	1·0000	3·989	3·989	3·989

REFERENCES

[1] C. S. Cheung, M. A. Cooper and S. L. Manatt, *Tetrahedron*, **27**, 689–700 (1971)
[2] J. A. Pople, D. P. Santry and G. A. Segal, *J. Chem. Phys.* **43** *S*, 129 (1965)
[3] J. A. Pople and G. A. Segal, *Ibid.* **43** *S*, 136 (1965); *Ibid.* **44**, 3289 (1966)
[4] M. A. Cooper and S. L. Manatt, *J. Am. Chem. Soc.* **92**, 1605 (1970)
[5] G. L. Hardgrave, L. K. Templeton and D. H. Templeton, *J. Phys. Chem.* **72**, 668 (1968)
[6] J. L. Lawrence and S. G. G. Macdonald, *Acta. Cryst.* **B25**, 978 (1968)
[7] H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.* **42**, 756 (1946)
[8] R. D. Rieke, C. F. Meares and L. I. Rieke, *Tetrahedron Letters* 5275 (1968)
[9] R. D. Rieke, W. E. Rich and T. H. Ridgway, *Ibid.* 4381 (1969)
[10] A. Streitwieser, G. R. Ziegler, P. C. Mowerey, A. Lewis and R. G. Lawler, *J. Am. Chem. Soc.* **90**, 1357 (1968)
[11] R. A. Finnegan, *J. Org. Chem.* **30**, 1333 (1965)
[12] M. A. Cooper and S. L. Manatt, *J. Am. Chem. Soc.* **91**, 6325 (1969)
[13] M. A. Cooper, D. D. Elleman, C. D. Pearce and S. L. Manatt, *J. Chem. Phys.* **53**, 2343 (1970)
[14] M. A. Cooper and S. L. Manatt, *J. Am. Chem. Soc.* **92**, 4646 (1970)
[15] M. A. Cooper and S. L. Manatt, *Org. Magn. Resonance* **2**, in press (1970)
[16] W. H. Mills and I. G. Nixon, *J. Chem. Soc.* 2510 (1930)
[17] J. A. Pople and D. P. Santry, *Mol. Phys.* **8**, 1 (1964)
[18] M. Barfield and D. M. Grant, *Advances in Magnetic Resonance*, (Edited by J. S. Waugh) Vol. 1, pp. 149–192. Academic Press, New York, N.Y. (1965)
[19] M. Barfield and B. Chakrabarti, *Chem. Revs.* **69**, 757 (1969)
[20] J. T. Gerig and J. D. Reinheimer, *Org. Mag. Resonance* **1**, 239 (1969)
[21] C. S. Cheung, M. A. Cooper and S. L. Manatt, unpublished work
[22] D. J. Bertelli, T. G. Andrews and P. O. Crews, *J. Am. Chem. Soc.* **91**, 5286 (1969)

TABLE 4. OBSERVED AND CNDO/2 CALCULATED PMR COUPLING CONSTANTS

Molecule	Nuclei	J_{obs} (Hz)	$J_{CNDO/2}$ (Hz)
	1,2	7·56[a]	4·14
	1,3	1·38	0·81
	1,4	0·68	0·25
	1,2	8·30[b]	4·44
	1,3	1·21	0·84
	1,4	0·75	0·33
	2,3	6·84	3·92
	1,2	6·89[c]	3·89
	1,3	0·82	0·66
	1,4	1·00	0·77
	2,3	8·25	4·81
	1,2	6·04[c]	3·51
	1,3	0·33	0·40
	1,4	1·85	1·15
	2,3	7·63	4·47
	1,2	7·36[c]	4·19
	1,3	1·00	0·69
	1,4	1·03	0·77
	2,3	7·79	4·86
	1,4	—	1·35
	1,2	7·59[c]	4·17
	1,3	1·17	0·79
	1,4	0·48	0·43
	2,3	7·20	4·25
	1,2	7·56[c,d]	4·17
	1,3	1·34	0·88
	1,4	0·57	0·30
	2,3	7·35	4·10
	1,2	3·70[e]	1·77
	4,5	9·50	5·70
	4,6	1·10	0·71
	4,7	0·50	0·15
	5,6	10·00	6·15
	5,7	1·00	0·56

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

[b] Experimental data from Ref 2.

[c] Experimental data from Ref 1.

[d] Experimental data are for 9,10-dihydroanthracene.

[e] Experimental data from Ref 22.