Recrystallization from cyclohexane gave green crystals: mp 218–220 °C; ^{1}H NMR (250 MHz) δ 8.25 (m, 2, 1-, 12-ArH), 7.58 (m, 2, 4-, 9-ArH), 7.48 (m, 4, 2-, 3-, 10-, 11-ArH), 7.40 (s, 2, 13-, 14-ArH), 7.16 (s, 2, 5-, 8-ArH), 7.05 (s, 2, 6-, 7-ArH), and 0.02 (s, 6, $-CH_3$); ^{13}C NMR (15.1 MHz) δ 138.5, 136.2, 131.6, 129.5 (quaternary aryl C), 128.2, 127.7, 127.2, 127.1, 124.4, 123.2, 116.7 (aryl CH), 39.5 (bridge >C<), 19.2 ($-CH_3$); $MH^{+\cdot}$ (CI) *m/e* 333 (100), 317 (20), 302 (13); UV (cyclohexane) λ_{max} (log ϵ_{max}) 733 nm (1.21), 716 (1.43), 703 (sh, 1.57), 683 (sh, 2.01), 654 (2.37), 615 (2.25), 567 (1.96), 460 (sh, 3.70), 435 (sh, 3.82) 417 (4.04), 397 (4.15), 360 (4.97), 343 (4.83), 284 (sh, 4.13), 272 (4.31), 258 (4.30), and 207 (4.66). Anal. ($C_{26}H_{20}$) C, H.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Victoria for financial support. We also thank Dr. Keith Dixon of this department for help in simulating NMR spectra.

Registry No. **1**, 66093-76-3; **4**, 66093-77-4; **6**, 66093-78-5; **7**, 80664-93-3; **8**, 54811-08-4; **9**, 54811-12-0; **10**, 80664-94-4; **11**, 80721-49-9; **14**, 956-84-3; **21**, 80664-95-5; **22**, 80664-96-6; **23**, 36015-77-7; **24**, 66093-80-9; **25**, 80664-97-7; **26**, 80664-98-8; **27**, 72094-95-2; **28**, 72094-96-3; **29**, 189-55-9; **30**, 189-64-0; **31**, 80679-91-0; **32a**, 80664-99-9; **35**, 80679-93-2; **38**, 5334-79-2; **39**, 19930-47-3; **40**, 80665-00-5; **41**, 80665-01-6; **42**, 80665-02-7; **43**, 66093-81-0; **44**, 66093-75-2; **45**, 66328-44-7; **46**, 80665-03-8; **47**, 80734-45-8; **48**, 80679-94-3; **49**, 80679-95-4; **50**, 80679-97-6; *syn*-2,11-dithia[3.3]metacyclophane, 72150-45-9; *syn*-9,18-dimethyl-2,11-dithia[3.3]metacyclophane, 26787-71-3; *anti*-9,18-dimethyl-2,11-dithia[3.3]metacyclophane, 26787-70-4; *syn*-2,13-dithia[3]metacyclo[3](1,3)naphthalenophane, 72150-49-3; *syn*-11,20-dimethyl-2,13-dithia[3]metacyclo[3](1,3)naphthalenophane, 80734-46-9; *anti*-11,20-dimethyl-2,13-dithia[3]metacyclo[3](1,3)naphthalenophane, 66093-79-6; *anti*-dimethylbenzo(10,11-*a*)-2-thia[2.3]metacyclophane, 65649-30-1; thiourea, 62-56-6.

Toward the Understanding of Benzannelated Annulenes: A Simple Correlation of the Diatropicity of Several Benzannelated Dihydropyrenes in Terms of Bond Order Deviations with Predictions for Other Benzannulenes[1]

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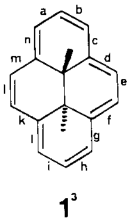
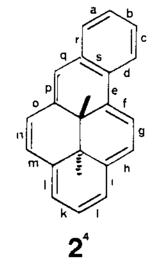
Abstract: A linear relationship between the chemical shift shielding of the internal protons of the series of benzannelated dihydropyrenes **1–5** and the average deviation of π-SCF bond order of the macrocyclic ring from the Hückel [14]annulene value of 0.642 has been determined empirically. A similar relationship was obtained for selected internal and external protons of the series of Nakagawa's benzannelated dehydro[14]annulenes **28–30**. The equations thus determined have been used to predict 18 known and 29 unknown chemical shifts of other benzannelated annulenes. Most of the known shifts agree with those calculated to <0.5 ppm. These results suggest that bond localization caused by benzo- or other aromatic ring annelation is the principal determinant of the strength of the macrocyclic ring current in these compounds.

In the three accompanying preceding papers, we have described the syntheses and properties of the benzannelated dihydropyrenes[2] **2–5**. These properties have been comparedd to each other and to those of the parent dihydropyrene[2] **1**. We have shown that the diatropicity order as evidenced by the shielding of the internal methyl protons (and carbons) is in the order **1** < **5** < **2**, **3** < **4** and we have interpreted this in terms of bond localizations as predicted by consideration of simple Kekulē structures,

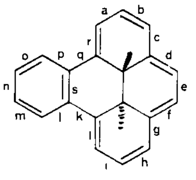
In this paper we wish to show that the diatropicity of these systems can be correlated quantitatively (though empirically) by means of simple π-SCF bond order calculations and that the results can be used predictively in this as well as other systems.



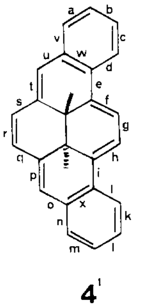
1[3]



2[4]



3[5]



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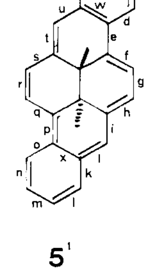

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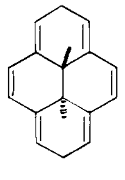

6[3]

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(1) Benzannelated Annulenes. 9. For part 8, see: R. H. Mitchell, R. V. Williams, and T. W. Dingle, *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) For *Chemical Abstract* names and numbering see the preceding papers.[1,4,5] Since we require to identify each bond we have chosen to use the lettering system given in this paper.

(3) V. Boekelheide and J. B. Phillips, *J. Am. Chem. Soc.*, **89**, 1695 (1967); R. H. Mitchell and V. Boekelheide, *ibid.*, **96**, 1547 (1974).

(4) R. H. Mitchell, R. J. Carruthers, L. Mazuch, and T. W. Dingle, *J. Am. Chem. Soc.*, this issue.

(5) R. H. Mitchell, J. S. H. Yan, and T. W. Dingle, *J. Am. Chem. Soc.*, this issue.

0002-7863/82/1504-2571$01.25/0

Table I. Hückel MO Bond Orders (×10³) ($\overline{P}_\mu$) and π-SCF Bond Orders (×10³) (P_μ) for Compounds 1-5

	1		2		3		4		5	
bond (μ)	$\overline{P}_\mu$	P_μ	$\overline{P}_\mu$	P_μ	$\overline{P}_\mu$	P_μ	$\overline{P}_\mu$	P_μ	$\overline{P}_\mu$	P_μ
a	642	647	708	713	597	550	698	696	716	735
b	642	639	611	612	676	729	621	629	602	586
c	642	636	708	711	611	553	697	694	716	734
d	642	650	571	574	669	713	583	596	561	545
e	642	636	529	481	614	567	503	438	550	543
f	642	639	704	745	669	715	735	794	674	672
g	642	647	597	552	611	553	557	489	629	635
h	642	647	676	719	676	729	735	794	629	621
i	642	639	611	558	597	550	503	438	674	680
j	642	636	669	717	704	748	583	596	550	545
k	642	650	614	573	529	477	697	694	561	545
l	642	636	669	712	571	580	621	629	716	735
m	642	639	611	553	708	707	698	696	602	586
n	642	647	676	731	611	617	581	595	716	734
o			597	538	708	707	507	443	561	545
p			704	752	571	580	726	792	550	543
q			529	484	529	477	571	488	674	672
r			571	575	704	748	706	780	629	635
s			502	538	502	537	571	488	629	621
t							726	792	674	680
u							507	443	550	545
v							581	595	561	545
w							513	554	490	508
x							513	554	490	508
$\Delta P_\mu = \Sigma_m \lvert(P_\mu - 642)\rvert$		72		1279		1303		2009		584
$m = \Sigma_\mu$		14		13		13		12		12
$\Delta r = \Delta P_\mu / m$		5.143		98.385		100.231		167.417		48.667
$\delta = \delta_{CH_3}$(annulene)		−4.25		−1.60		−1.85		+0.02		−3.58
$\Delta\delta = 0.97 - \delta$		5.22		2.57		2.82		0.95		4.55
$\Delta\delta_{calcd}$ (eq 1)		5.39		2.83		2.77		0.93		4.19

Since the pioneering work of Pauling[6] and London,[7] considerable work has been done on the calculation of the nuclear magnetic resonance spectra of aromatic hydrocarbons.[8] Unfortunately, these calculations appear fairly formidable to the average chemist. However, it is quite clear[8d] that, for all sizes of rings, the magnitude of the ring current is partially reduced if bond alternation occurs. Several attempts have been to calculate the dependence of the ring current on the bond alternation which is usually represented by taking two different values for the resonance integral, β. Indeed, the prediction that bond alternation in the higher unsubstituted annulenes will occur naturally has led to much stimulating discussion and synthesis.[9] Haddon[8i] has stated that bond alternation should form a fairly close relationship with resonance energies. Subsequently,[10] he has shown that resonance energies and ring currents are also interrelated in simple annulenes. Although considerable progress has been made in this area, the relationships obtained are fairly complex.

Since benzannelation of an annulene causes bond localization (alternation) in the macrocyclic ring, it seems reasonable then

Table II. Bond Orders (×10³), P_μ, and Ring Current Shielding Calculations for Compounds 7-**10** [See Table I for Definitions]

	P_μ			
bond (μ)	7	8	9	**10**
a	610	670	652	670
b	720	603	687	601
c	567	474	583	477
d	488	793	495	788
e	783	490	773	497
f	503	570	518	559
g	520	667	495	683
h	714	629	749	605
i	583	646	532	
j	692	532	757	
k	586	648	473	
l	693	531	579	
m	599	525	708	
n	686	518	614	
o	583		711	
p	702		576	
q	574		483	
r	711		756	
s	541		547	
t	457		710	
u	575		588	
v	716		636	
w	558		468	
x	561		808	
y			454	
z			621	
aa			526	
bb			534	
cc			527	
dd			560	
ee			472	
ff			538	
IV	854	260	1134	570
m	13	12	11	10
Δr	65.692	21.667	103.091	57
$\Delta\delta_{calcd}$	3.72	4.94	2.70	3.96
$\Delta\delta_{found}$	3.75	5.20	2.3	4.2

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(6) L. Pauling, *J. Chem. Phys.*, **4**, 673 (1936).

(7) F. London, *J. Phys. Radium*, **8**, 397 (1937).

(8) See, for example: (a) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958); (b) J. A. Pople, *Mol. Phys.*, **1**, 175 (1958); (c) R. McWeeny, *ibid.*, **1**, 311 (1958); (d) H. C. Longuet-Higgens and L. Salem, *Proc. R. Soc. London*, Ser A, **257**, 445 (1960); (e) N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962); (f) L. Salem, J. A. Pople, and K. G. Untch, *Tetrahedron*, **88**, 4811 (1966); (g) T. Nakajima and S. Khoda, *Bull. Chem. Soc. Jpn.*, **39**, 804 (1966); (h) C. W. Haigh and R. B. Mallion, *Mol. Phys.*, **18**, 737, 751 & 767 (1970); (i) R. C. Haddon, *Tetrahedron*, **28**, 3613, 3615 (1972); (j) G. Ege and H. Vogler, *Tetrahedron*, **31**, 569 (1975); **32**, 1789 (1976); H. Vogler, *J. Am. Chem. Soc.*, **100**, 7464 (1978); *Tetrahedron*, **35**, 657 (1979); (k) H. G. F. Roberts, *J. Magn. Reson.*, **29**, 7 (1978); (l) C. A. Coulson and R. B. Mallion, *J. Am. Chem. Soc.*, **98**, 592 (1976); J. A. N. F. Gomes and R. B. Mallion, *J. Org. Chem.*, **49**, 719 (1981), and references quoted therein.

(9) See, for example: M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685, 692 (1965); M. J. S. Dewar and C. De Llanos, *ibid.*, **91**, 789 (1969); M. J. S. Dewar, M. C. Kohn, and N. Trinajstic, *ibid.*, **93**, 3437 (1971); M. J. S. Dewar, "Aromaticity", Special Publication No. 21. The Chemical Society, London, 1967, p 177; H. C. Longuet-Higgins and L. Salem, *Proc. Ry. Soc. London, Ser. A*, **251**, 172 (1959); **257**, 445 (1960).

(10) R. C. Haddon, *J. Am. Chem. Soc.*, **101**, 1722 (1979).

Table III. Bond Orders ($\times 10^3$), P_μ, for a Series of Unknown Annelated Derivatives of **1** and Calculations of Methyl Proton Shieldings Using Equation 1

bond	$P_\mu \times 10^3$														
(μ)	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**
a	577	693	587	639	589	577	749	585	576	563	795	630	748	643	593
b	739	632	732	685	724	747	575	700	741	758	468	612	526	622	689
c	541	694	547	607	561	529	749	583	535	514	809	688	756	671	581
d	556	595	544	423	518	571	527	688	569	604	420	524	488	567	701
e	677	439	672	818	732	657	576	596	643	613	675	613	516	488	582
f	616	785	633	432	519	454	652	689	662	527	559	606	774	794	711
g	654	505	505	602	559	767	457	581	601	678	535	513	499	476	529
h	638	763		692	727	528	766	703	705	629	743	759	561	574	508
i	625	505		627	587	747	529	580	505	498	582	563	724	714	
j	665	765		699	736	531	738	718	626	460	742	758	604	615	
k	615	510		582	535	734	538	515	595		535	513	721	710	
l	685	783		475	571	546	733	508	518		557	605	569	582	
m	543	439		684	575	517	554	779	755		675	612	471	445	
n	549	600		480	535	484	730	492	567		419	525	497	579	
o	732	690		781	735		532	565	491		810	679	747	656	
p	584	636		528	504		750	721	468		468	498	536	533	
q	738	688		545	499		515	608	504		525	465	582	561	
r	534	605		557			774	718			493		553		
s	576	427					456	573							
t	584	820					653	462							
u	527	429					577	532							
v	743	601					527	709							
w	495	556					515	555							
x	497	552					487	562							
W	496	1946	548	1628	950	1566	1552	877	670	656	2235	720	1480	404	867
m	12	12	12	10	10	13	13	13	12	12	12	12	12	12	13
Δr	41.33	162.17	45.67	162.80	95.00	120.46	119.38	67.46	55.80	54.67	186.25	60.00	123.33	33.67	66.69
$\Delta\delta_{\text{calcd}}$	4.40	1.07	4.28	1.05	2.92	2.22	2.25	3.68	4.00	4.03	0.41	3.88	2.14	4.61	3.70

that the strength of the ring current in the macrocyclic ring will be related in some way to the degree of bond localization present. Here a theoretical analysis is likely to be even more complicated than for simple annulenes. On the on hand, for many purposes, a simple correlation between the observed quantity, in this case the chemical shift of the protons, and some easily calculated quantity can be useful experimentally and suggestive theoretically. During discussions at the Third International Symposium of Novel Aromatics (ISNA III, San Francisco, 1977) Professors B. Andes Hess, Jr., and L. J. Schaad (Vanderbilt University) provided us with a possible correlation. They took selected[11] HMO bond orders of **1**, **2**, **4**, and **5** and used the standard deviation of the bond order from the average as a measure of the delocalization.[12] We have now developed and extended these ideas as outlined below.

Result and Discussion

One disadvantage of HMO calculations is that they do not differentiate between isomeric compounds such as **2** and **3**. Also because of the neglect of the electron repulsion integrals, $\gamma_{\mu,\nu}$, HMO calculations under estimate the amount of bond localization in a benzannulene as compared to π-SCF calculations. This can be seen for example by comparison of bonds a–i and **3** given in Table I, which presents both HMO and π-SCF bond orders for the standard compounds of this study, **1–5**. Moreover, the final correlation using HMO bond orders is not as good.[13] Since we wanted to use any results of this study as a predictive tool, we did not want to place too many restrictions as to which bonds should be included in our calculations. Thus, we have used π-SCF bond orders throughout and have excluded from the calculations only those bonds common to two rings. The bond orders were calculated with use of Pariser–Parr–Pople (PPP) π-electron theory,[13] with the same parameters[14] as Cremer and Günther[15] so that results reported in our examples will be comparable to results in their systems. Some calculations have been done with use of other parameters suggested in the literature. These lead to slight changes in the π-bond orders, which change slightly the details, but not the substance, of our procedure.

In Table I, which presents the bond orders ($\times 10^3$), P_μ, for the molecules **1–5**, the sum (ΔP_μ) of the moduli of the deviations of bond order from the "ideal" or perfectly delocalized Hückel bond order value for a [14]annulene of 0.642 is given for *the macrorings* of **1–5** *excluding* only the benzannelating ring-fused bond(s), e.g., s in **2**, **3** or w, x in **4**, **5**. We thought it reasonable to exclude such bonds since they are involved in both the 6π and 14π rings, may have opposing ring currents, and may introduce structural effects.[16]

Thus $\Delta P_\mu = \sum_m |(P_\mu - 642)|$ where m = the number of bonds of the macroring-benzannelating ring-fused bonds. The average deviation of bond order, Δr, was then calculated as the mean value of ΔP_μ, i.e.

$$\Delta r = \Delta P_\mu / m$$

This deviation Δr was plotted against $\Delta\delta$, where

$$\Delta\delta = \delta_{\mathrm{CH_3}}(\mathbf{6}) - \delta_{\mathrm{CH_3}}(\text{annulene}) = 0.97 - \delta$$

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(11) The central bonds far away from the annelating rings were compared, i.e., d, e, f in **1** and f, g, h in **2**, **4**, and **5**.

(12) See: R. H. Mitchell, *Isr. J. Chem.*, **20**, 294 (1980).

(13) An alternate approach may be to use the self-consistent HMO method where the value of β is adjusted to be self consistent with the bond orders calculated (and by implication with the bond lengths used). This leads to values of the bond order rather similar to π-SCF calculations. See: C. A. Coulson and A. Jolebiewski, *Pror. Phys. Soc.*, **78**, 1310 (1961); K. Vasudevan and W. G. Laidlaw, *Collect. Czech., Chem. Commun.*, **34**, 3225, 3610 (1969).

(14) See: J. N. Murrell and A. J. Harget in "Semiempirical Self Consistent Field Molecular Orbital Theory of Molecules", John Wiley, London, 1972, Chapter 2, for a discussion of π-electron theory. Idealized geometries (C–C bond length = 140 pm; CCC bond angle = 120°) were used. The resonance integral, $\beta_{\mu,\nu}$, was assigned a value of -2.366 eV for nearest neighbors. All two-electron integrals, $\gamma_{\mu,\nu}$, were calculated by using the Mataga–Nishimoto relationship $\gamma_{\mu,\nu} = 1.4397/[R + (2.8794/(\gamma_{\mu,\mu} + \gamma_{\nu,\nu}))]$ eV with a value of 10.67 eV used for $\gamma_{\mu,\mu}$ for the carbon atom. Other parametrizations gave very similar values for bond orders.

(15) D. Cremer and H. Günther, *Justus Liebigs Ann. Chem.*, **763**, 87 (1972).

(16) For completeness, we also derived the eq A, which omits the bonds q and e as well as s in **2**, for example, in the calulation of $\Delta r'$. This could be justified on the assumption that structurally these bonds would be most affected by ring fusion, and could introduce anisotropy effects. However, this

$$\Delta\delta' = 5.297 = 0.0292\Delta r' \qquad \rho = 0.998 \qquad \text{(A)}$$

equation would be less useful for higher annelated systems, since most bonds would be excluded from the calculation.

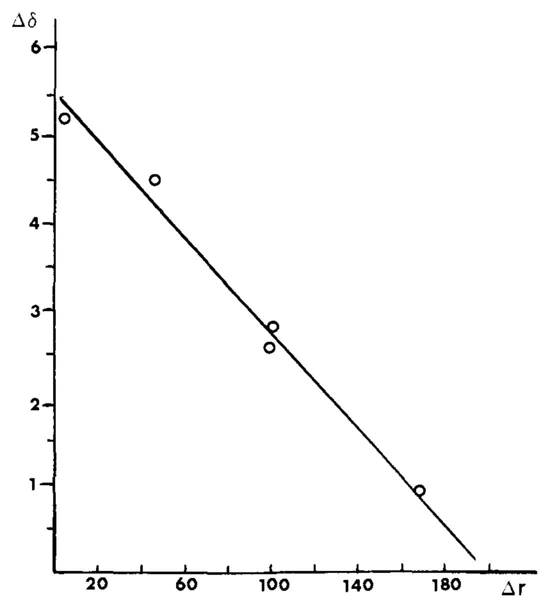
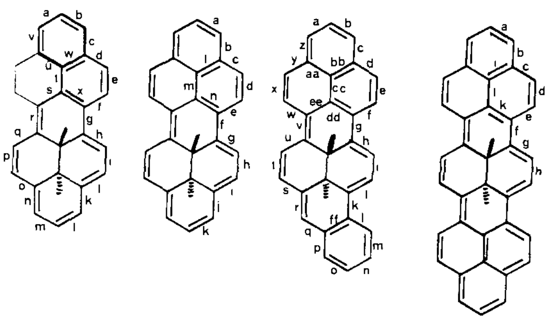


Figure 1. Plot of chemical shift shielding (Δδ) vs. average bond order deviation (Δr) for annulenes **1**–**5**.



δ(CH₃)	7	8	9	10
CALC.	-2·75	-3·97	-1·73	-2·99
FOUND	-2·78	-4·19 -4·28	-1·35 -1·41	-3·20

Figure 2. Calculated and determined chemical shifts for **7**–**10**.

i.e., Δδ is the shielding of the internal methyl protons of the annulene from those of the unconjugated model **6**.[3] This plot gave a reasonably good straight line, Figure 1.

A least-squares fit gave

$$\Delta\delta = 5.533 - 0.02752\Delta r \qquad (1)$$

with a correlation coefficient $\rho = 0.9902$. Values of Δδ, calculated using eq 1, are also shown in Table I as $\Delta\delta_{\text{calcd}}$ and provide examples of the good fit.

Since the various theoretical relationships between ring-current shielding and the degree of bond localization in a system are rather complex, there might be no reason to expect a linear relationship between these variables. However, the results obtained here suggest that there is one. While we have not yet been able to theoretically derive this relationship, we have been able to test it further. Clearly if such a relationship is to have any value, it must be able to predict reasonably well results for new systems. We thus decided to test eq 1 on the higher annelated annulenes **7**–**10**, which had not at the time been prepared.

Table II presents the results of these calculations for **7**–**10**, using eq 1. The calculated and recently determined[17] chemical shifts of the internal methyl protons are shown in Figure 2. Clearly the agreement is very good and provides considerable support for the orginal hypotheses.

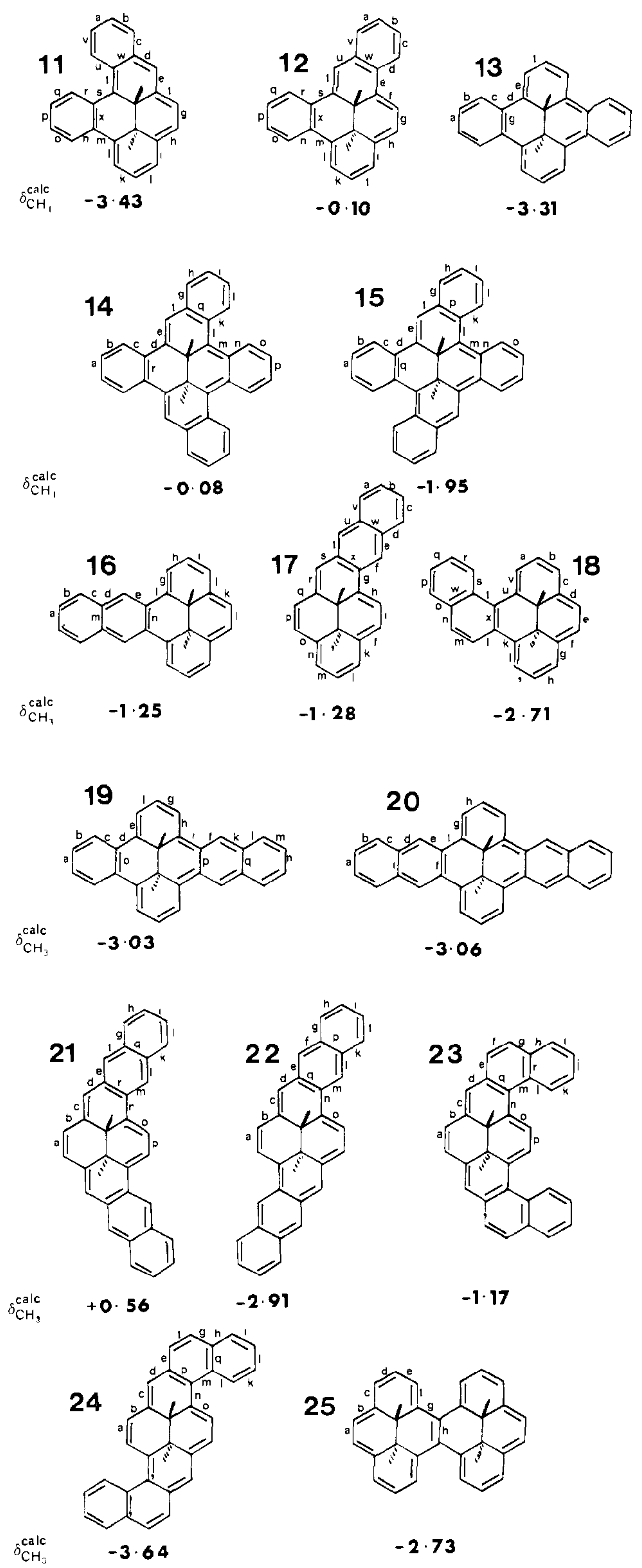


Figure 3. Calculated internal methyl proton shifts for a series of unknown annelated derivatives of **1**.

Indeed it is worthwhile commenting as to why the method appears to work so well. Consider the internal methyl protons of **1**–**10** relative to those in **6**. One major factor that affects the shielding of these protons is the macrocyclic ring current, and this effect is large, because the protons are close to the center of the

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(17) Ramanathan Mahadevan, Ph.D. Thesis, University of Victoria. To be submitted July 1981.

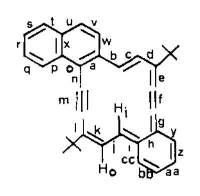
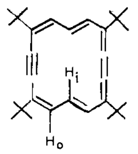
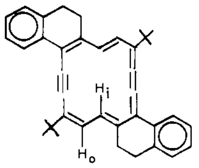
COMPOUND	$\Delta\delta_i$			δ_i			$\Delta(\delta_o-\delta_i)$			δ_o		
	CALCULATED EQ(4)	CALCULATED EQ(6)	FOUND	CALCULATED EQ(4)	CALCULATED EQ(6)	FOUND	CALCULATED EQ(5)	CALCULATED EQ(7)	FOUND	CALCULATED EQ(5)	CALCULATED EQ(7)	FOUND
 **31**	7.82	8.05	7.65	-2.22	-2.45	-2.05	11.82	12.16	11.55	9.60	9.71	9.50
 **26**	10.83	----	12.04	-5.23	-----	-4.39	16.20	-----	13.81	10.97	-----	9.42
 **27**	9.76	9.68	9.52	-4.16	-4.08	-3.47	14.65	14.54	12.99	10.49	10.46	9.07

Figure 4. Comparison of actual and calculated shifts for H_i and H_0 of **26**, **27**, and **31**.

Table IV. Calculated Bond Orders (X10^3), P_μ (All Bonds Equal, 139.7 pm) and $\widetilde{P}_\mu$ (Central Shortened Bond, 120.8 pm) for 26-31

bond	26		27		28		29		30		**31**	
(μ)	P_μ	$\widetilde{P}_\mu$	P_μ	$\widetilde{P}_\mu$	P_μ	$\widetilde{P}_\mu$	P_μ	$\widetilde{P}_\mu$	P_μ	$\widetilde{P}_\mu$	P_μ	$\widetilde{P}_\mu$
a	638	629	655	627	539	548	563	578	532	551	511	533
b	649	678	626	650	477	483	517	519	562	560	594	587
c	640	566	658	614	750	727	716	696	668	651	631	618
d	639	730	628	690	548	588	584	622	634	669	673	702
e			656	551	728	641	691	605	636	553	591	513
f			597	747	548	669	595	706	657	751	709	787
g			605	526	720	636	649	571	580	508	513	452
h			347	360	567	606	556	583	445	465	522	533
i			623	619	717	699	704	695	582	574	514	516
j			676	677	551	549	574	566	711	715	709	686
k			661	670	734	755	708	735	615	612	595	635
l					537	472	571	500	714	716	672	583
m					755	815	715	790	573	572	621	729
n					475	421	530	464	477	481	612	534
o					580	596	462	478	791	793	435	457
p					709	703	573	567	491	487	587	578
q					615	618	717	721	561	557	706	711
r					708	710	608	606			619	615
s					578	574	720	722			710	712
t							566	565			579	576
u							491	493			467	472
v							780	783			800	799
w							506	501			480	478
x							556	553			564	559
y							346	360			561	581
z							624	619			723	714
aa							675	676			600	605
bb							661	660			722	721
											561	558
W	58		310	342	1343	1163	898	810	396	384	660	564
m	14		14	14	13	13	13	13	12	12	12	12
Δr	4.14		22.14	24.43	103.31	89.46	69.08	62.31	33.00	32.00	55.00	47.00

ring. The direct deshielding effect of the added benzannelating rings can be estimated from the results of Johnson and Bovey[8a] and is small (e.g., ca. 0.1 ppm for **2**) principally because the protons in question are well out from the center of the benzannelating ring current.[18] Local anisotropy changes on benzannelation would also be expected to be small for the internal methyl protons (though not for the external protons),[8j] since these protons are well insulated from the π network by the σ bridges and changes in anisotropy due to the σ system are not expected to be very significant due to the similarities around the bridge of the various structures.[20] As we originally stated.[4] these special properties of the dihydropyrene ring system make it an excellent probe of ring current effects.

Table III gives the bond orders for and makes predictions of

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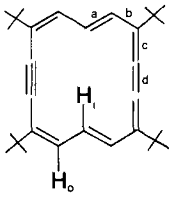
(18) In support of this calculation we find[19] that the methyl protons of 2-phenyl-**1** are at δ −4.00 and −4.03.

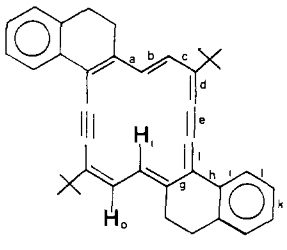
(19) R. H. Mitchell and R. V. Williams, unpublished results.

the chemical shifts in a series of as yet unknown annelated derivatives of **1** (shown in Figure 3). We are attempting the synthesis of some of some of these to provide further verification of our correlation.

In principle, our method should be applicable to any series of benzannelated annulenes, providing a suitable NMR probe is present. Nakagawa's extensive work[12] on a series of annelated derivatives of **26** provides data for a further test of our approach.

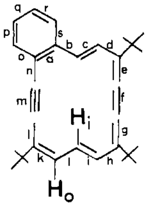


26



27

In the parent **26**, H_i appear[21] at δ -4.39 and H_o at δ 9.42, clearly indicating the existence of a strong diamagnetic ring current. However, in this series of compounds, it must be expected that the inner protons H_i will be affected by anisotropy effects more than the internal methyl protons of **1**. Evidence for this can be found from the ^1H NMR data[22] of **27** in which H_i appear at δ -3.47, 0.92 ppm deshielded from those in **26**, a much larger effect than observed in the dihydropyrene series.[18,19] Therefore, such good agreement between the calculated and observed values as found with our compounds might not be expected. Nakagawa's compounds present a further problem, namely that of the shortened central bonds. Two approaches to deal with this are feasible: (i) the shortened bonds can be neglected entirely, on the basis that they are mainly constraints on the σ system and will not much affect *differences* in π-bond order between analogues of **26**, and (ii) actual bond orders can be derived on the basis of the known[23] geometry of the parent of **26**, and then the changes in π-bonds order can be calculated by subtracting these values from those obtained for the parent. We have tried both approaches and both are satisfactory, though the first is much simpler to execute. The compounds used as standards to derive the equations were **28**,[21] **29**,[22] and **30**.[22]



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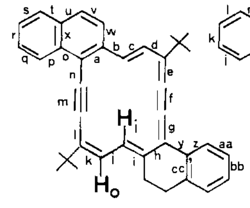

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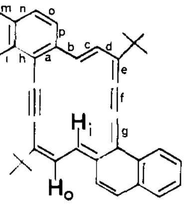
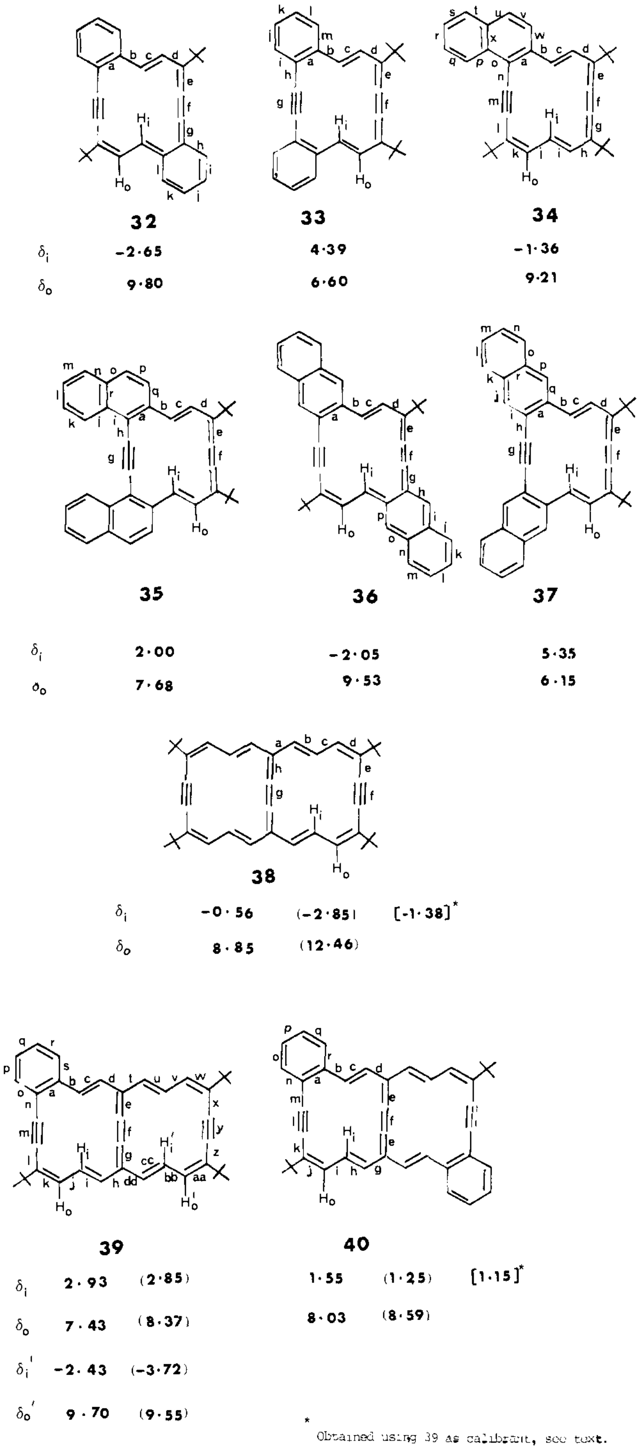


30

	28	29	30
δ_i	0·71	-1·53	-3·45
δ_o	8·33	9·17	10·22
$\Delta\delta_i$	4·89	7·13	9·05
$\delta_o - \delta_i$	7·62	10·70	13·67



	32	33	34
δ_i	-2·65	4·39	-1·36
δ_o	9·80	6·60	9·21

	35	36	37
δ_i	2·00	-2·05	5·35
δ_o	7·68	9·53	6·15

	38		
δ_i	-0·56	(-2·85	[-1·38]*
δ_o	8·85	(12·46)	

	39		40		
δ_i	2·93	(2·85)	1·55	(1·25)	[1·15]*
δ_o	7·43	(8·37)	8·03	(8·59)	
δ_i'	-2·43	(-3·72)			
δ_o'	9·70	(9·55)			

* Obtained using 39 as calibrant, see text.

Figure 5. Calculated (and found) chemical shifts δ_i and δ_o based on data in Table V and eq (2) and (3) for a series of derivatives of **26**.

Table IV shows the calculated bond orders ($\times 10^3$), (i) P_μ, based on π-SCF calculations as above, assuming all bond lengths are equal, for **26–31**, and (22) $\bar{P}_\mu$[25], based on a shortened central bond of 120.8 pm with all others being 139.7 pm. Other terms have the meanings defined above.

In the first case, where equal bond lengths were used, a least-squares fit on the plot of $\Delta\delta_i$, where

$$\Delta\delta_i = 5.60 - \delta_i$$

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(20) Indeed even if the bonds adjacent to the ring fusion points are omitted from the calculations, as in eq A,[16] the resulting values of δ calculated for **7** (-2.65), **8** (-3.99), **9** (-1.60), and **10** (-3.17) are not markedly changed. Omission of the parent **1** from the data used to define eq 1, gives

$$\Delta\delta = 5.821 - 0.0299\Delta r \qquad \text{(B)}$$

which when used to calculate δ for compounds **2–10** gives values less than 0.2 ppm different from those above. This indicates that anisotropy changes caused by the fused rings are small.

(21) K. Sakano, S. Akiyama, M. Iyoda, and M. Nakagawa, *Chem. Lett.*, 1019, 1023 (1978).

(22) M. Iyoda, M. Morigaki, and M. Nakagawa, *Tetrahedron Lett.*, 817, 3677 (1974).

(23) N. A. Bailey and R. Mason, *Proc. Chem. Soc.*, 180 (1963); *Proc. Ry. Soc. London, Ser. A*, **290**, 94 (1966).

(24) A. Yasuhara, M. Iyoda, T. Satake, and M. Nakagawa, *Tetrahedron Lett.*, 3931 (1975).

(25) To calculate $\Delta\bar{r}$, each corresponding bond order of **26** is substracted from the appropriate bond order of the annulene under study, i.e.

$$\Delta\bar{P}_\mu = \sum_m |(P_{\mu\mathrm{annulene}} - P_{\mu 26})|$$

Table V. Calculated π-SCF Bond Orders (X10^3), P_μ, and Ring Current Shielding Parameters for a Series of Annelated Derivatives of 26

	P_μ									
bond (μ)	32	33	34	35	36	37	38	39		40
a	506	557	563	587	463	494	520	553		548
b	543	437	516	477	525	421	725	437		449
c	674	787	719	755	681	801	561	806		792
d	634	504	579	539	628	486	714	451		470
e	627	769	750	740	623	783	572	571		612
f	675	496	579	531	682	478	704	688		641
g	543	825	693	772	524	841	710	567		495
h	546	421	596	483	613	402	549	468		755
i	734	605	690	477	605	685		775		521
j	584	690	582	566	513	553		502		756
k	733	634	704	723	758	538		771		513
l	546	691	575	606	563	741		497		776
m		599	714	726	758	584		788		453
n			531	559	514	742		440		591
o			468	503	605	536		597		699
p			574	769	613	555		694		626
q			717	520	498	676		631		698
r			608	551		527		692		592
s			720					598		
t			566					558		
u			491					694		
v			780					592		
w			506					688		
x			556					598		
y								678		
z								599		
aa								690		
bb								589		
cc								698		
dd								551		
								H	H′	
W	572	2001	904	1517	694	2197	1162	1821	719	1523
m	12	12	13	12	12	12	14	13	14	13
Δr	47.67	166.75	69.54	126.42	57.83	183.08	83.00	140.08	51.36	117.15
$\Delta\delta_i$ (eq 2)	8.25	1.21	6.96	3.60	7.65	0.25	6.16	2.67	8.03	4.05
$\delta_o - \delta_i$ (eq 3)	12.45	2.21	10.57	5.68	11.58	0.80	9.41	4.50	12.13	6.48

i.e., $\Delta\delta_i$ is the shielding in ppm of the *internal* protons H_i from those in typical polyenes (δ 5.60), against Δr gave

$$\Delta\delta_i = 11.070 - 0.05911\Delta r \qquad (2)$$

with correlation coefficient $\rho = 0.9982$.

Similarly the difference in chemical shift of the *outer* (H_o) and *inner* (H_i) protons, $\delta_o - \delta_i$, gave

$$\delta_o - \delta_i = 16.552 - 0.08601\Delta r \qquad (3)$$

with correlation coefficient $\rho = 0.9997$. Application of these equations to the benzonaphtho analogue[24] **31** gave calculated values of $\delta_i = -2.22$ and $\delta_o = 9.60$ which are in remarkably good agreement (Figure 4) with those observed, δ −2.05 and 9.50, respectively. As can be seen from Figure 4 the values found for **26** are not in such good agreement, probably because of the large anisotropy changes, whereas the improved model **27** which has the fused, though not fully conjugated, rings gives much better agreement between calculated and observed chemical shifts.

In the second case where a shortened central bond (formally the acetylene bond) of 120.8 pm was assumed, eq (4) and (5) were obtained.[25] The calculated values of δ_i and δ_o for **26**, **27**, and **31**,

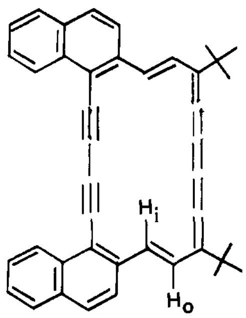
$$\Delta\delta_i = 11.447 - 0.07222\tilde{\Delta}r \qquad \rho = 0.9971 \qquad (4)$$

$$\delta_o - \delta_i = 17.104 - 0.1051\tilde{\Delta}r \qquad \rho = 0.9991 \qquad (5)$$

using eq 4 and 5, are also given in Figure 4. Interestingly the results are somewhat worse than those from eq 2 and 3 for **31**, but somewhat better for **27**, though the effect is only marginal. Clearly no real advantage is gained from eq 4 and 5, especially considering the more lengthy calculations involved in obtaining $\tilde{\Delta}r$.[25]

We have thus used eq 2 and 3 to calculate δ_i and δ_o for the series of compounds analogous to those of the dihydropyrenes of Figure 3, but derived from **26**, and these are given in Figure 5, based on the values of Table V. Some of these are worthy of comment:

A large difference in diatropicity is predicted between **32** and **33**, **30** and **35**, and **36** and **37**. Of these only **32** and **30** are known, but **32** was too unstable (compare **5**) to record a ^{1}H NMR spectrum.[24] The *cisoid*-dinaphtho)18]annulene **41**, analogous to **35**, is known,[22] however, and its internal protons appear at δ 1.81, a similar position to those calculated for **35** (δ 2.00) and very different from those of the transoid-isomer **30** at δ −3.45. The method even appears to work reasonably well for the multiply fused systems[26] **39** and **40**, though the parent **38**, like **26**, is not calculated well, presumably because of a fairly large anisotropy effect of the fused [14]π ring. If **39** rather than **28**–**30** is used as the calibrant, then $\Delta\delta_i = 13.124 - 0.07406\Delta r$, which for **40** yields $\Delta\delta_i = 4.45$, $\delta_i = 1.15$ in excellent agreement with that found. The result for **38**, $\delta_i^{calcd} = -1.38$, is also improved. Clearly, satisfactory results are obtained for Nakagawa's compounds, providing suitable model calibrants are used.



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[26] K. Sakano, S. Akiyama, M. Iyoda, and M. Nakagawa, *Chem. Lett.*, 1019, 1023 (1978).

Given these successes in these two series of compounds, it would seem reasonable that the method might be applied to other series of benzoannulenes or fused annulenes which have suitable internal NMR probes and for which enough examples exist to provide the necessary calibrations.

Conclusion

Our goal of showing a simple relationship between bond localization in a series of benzannulenes and strength of the ring current as measured by chemical shift shielding has been achieved. The linear relationship, though derived empirically by using examples of the series as calibrants, can be used predictively for other members of the series and in the bulk of the cases examined gives very good results (<0.5 ppm error).

As a result, the ring current shielding effect on the internal protons of many benzannulenes can now be reasonably estimated and depends primarily on the degree of bond localization in the macroring caused by the annelating ring. The relative positions of fusion by more than one annelating ring, as a consequence of their effect on bond localization, is of considerable importance and determines whether the macrocyclic ring will be highly diatropic or not.

Registry No. 1, 956-84-3; **2**, 66093-76-3; **3**, 65649-31-2; **4**, 66093-77-4; **5**, 66093-78-5; **7**, 80697-00-3; **8**, 80697-01-4; **9**, 80697-02-5; **10**, 80697-03-6; **11**, 80697-04-7; **12**, 80697-05-8; **13**, 80697-06-9; **14**, 80697-07-0; **15**, 80697-08-1; **16**, 80697-09-2; **17**, 80697-10-5; **18**, 80697-11-6; **19**, 80697-12-7; **20**, 80697-13-8; **21**, 80718-99-6; **22**, 80697-14-9; **23**, 80697-15-0; **24**, 80697-16-1; **25**, 80697-17-2; **26**, 65504-39-4; **27**, 54811-14-2; **28**, 80697-18-3; **29**, 54811-12-0; **30**, 54811-08-4; **31**, 80697-19-4; **32**, 80697-20-7; **33**, 80697-21-8; **34**, 80697-22-9; **35**, 80697-23-0; **36**, 80697-24-1; **37**, 80697-25-2; **38**, 65649-32-3; **39**, 80697-26-3; **40**, 80697-27-4.

ESR Study of the Attack of Photolytically Produced Hydroxyl Radicals on α-Methyl-D-glucopyranoside in Aqueous Solution[1]

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Contribution from the Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556.
Received August 28, 1981

Abstract: Six free radicals were observed when an aqueous solution of H_2O_2 and α-methyl-D-glucopyranoside was photolyzed using the in situ photolysis ESR method: a C6 primary hydroxyalkyl radical, a C2 secondary hydroxyalkyl radical, a C7 primary oxyalkyl radical, a Cl primary oxyalkyl radical, a C3 secondary hydroxyalkyl radical, and a C5 secondary oxyalkyl radical. The pH dependence of the concentration of these species, their reactions, stereochemical factors influencing radical stability, and comparison with product analysis studies are discussed.

Introduction

Carbohydrates are ubiquitous in nature, serving as energy sources, structural members, and components of nucleic acids in biological systems. Although the ionic chemistry of carbohydrates is well established,[2] the study of carbohydrate radiation and free-radical chemistry is a recent development.[3] Glucose (αGlu) is one of the most abundant monosaccharides in nature. Its derivative, α-methyl-D-glucopyranoside (αMeGlu), has the major structural features of αGlu, plus stability against anomerization in solution (see Figure 1). Single-crystal ESR and ENDOR studies of αGlu and αMeGlu have identified the free radicals generated by X-irradiation at 12 and 77 K and the thermally induced reactions of these transient intermediates.[4-7] In this report, these studies are extended to radicals generated by photolysis of αMeGlu/H_2O_2 aqueous solutions.

Experimental Section

Solutions in this study were freshly prepared with Millipore reagent-grade water, 40 mM αMeGlu (Aldrich), 0.678 M H_2O_2 (Fisher ACS), and 25 or 100 mM phosphate buffer (Fisher or Baker) with H_2SO_4 (Fisher ACS) or KOH (Baker) used to adjust pH as measured with a Sensorel glass electrode.

First-derivative ESR spectra were recorded with a steady-state in situ photolysis system using a Varian V-4502 ESR spectrometer with dual rectangular cavity, circulator, bias arm, and GaAs FET microwave amplifier. Microwave frequency was measured with a Hewlett-Packard 5245L counter with 5255A plug-in frequency converter. Microwave power was measured with an HP 431B power meter. Magnetic field measurements were made using a Varian Fieldial sweep unit, calibrated against the $(CH_3)_2\dot{C}OH$ radical. Relative signal intensities and g factors were calibrated against a Varian strong pitch sample (assumed g = 2.0028). Intensities were calculated as the product of first-derivative peak-to-peak line amplitudes multiplied by the square of peak-to-peak line width.

Nitrogen-saturated solutions were passed in a continuous flow system through a quartz ESR flat cell of 0.4 mm spacing and were photolyzed with unfiltered light from a 1-W Hanovia 977B-1 lamp. The temperature of the photolyzed sample was controlled by flowing thermostated N_2 gas past the flat cell, and was measured using a Doric DS-100-T3 thermocouple thermometer, with the sensor located at the flat cell outlet. The flow rate was typically 10 mL/min.

Results and Free-Radical Assignments

The ESR spectrum of 40 mM αMeGlu photolyzed at pH 5.5 and 8 °C is shown in Figure 2. Three major and three minor species, as indicated by stick figures, are present.

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[1] The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2274 from the Notre Dame Radiation Laboratory.

[2] See, e.g., Ferrier, R. J.; Collins, P. M. "Monosaccharide Chemistry"; Penguin Books: Middlesex, England, 1972, and references therein.

[3] See, e.g., von Sonntag, C. In "Advances in Carbohydrate Chemistry and Biochemistry", Vol. 37; Tipson, R. S., and Horton, D., (Eds.); Academic Press: New York, 1980, and references therein.

[4] Madden, K. P.; Bernhard, W. A. *J. Chem. Phys.* **1979**, *70*, 2431-37.

[5] Madden, K. P.; Bernhard, W. A. *J. Chem. Phys.* **1980**, *72*, 31-33.

[6] Madden, K. P.; Bernhard, W. A. *J. Phys. Chem.* **1979**, *83*, 2643-49.

[7] Madden, K. P.; Bernhard, W. A. *J. Phys. Chem.* **1980**, *84*, 1712-17.

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