IGLO Study of Benzene and Some of Its Isomers and Related Molecules. Search for Evidence of the Ring Current Model

U. Fleischer, W. Kutzelnigg,* P. Lazzeretti,† and V. Mühlenkamp

Contribution from the Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

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Abstract: IGLO calculations of the magnetic susceptibility tensors as well as of the ^{13}C and ^1H shielding tensors are performed and analyzed for benzene (1), the hypothetical cyclohexatriene (2) with alternating single and double bonds, some benzene isomers like fulvene (3), and other related molecules, including ethylene (8), the two 1,3-butadienes (9, 10), and eight hexatrienes (11–18). The susceptibilities of the noncyclic polyenes as well as the benzene isomers 4 and 5 are rather well described by an increment system both for the in-plane and out-of-plane components, that of benzene only for the in-plane component, while for the out-of-plane component there is an additional shielding of 42 ppm cgs, which is reduced to 33 ppm cgs in cyclohexatriene. The other two molecules of this study with a somewhat enhanced out-of-plane susceptibility are fulvene (13 ppm cgs) and cyclopentadiene (17 ppm cgs). Evidence is accumulated that the increased susceptibility in benzene comes from the π-electron system and is an indication of a nearly-free circular current in the π-system of benzene. This becomes particularly manifest if one uses the center of the molecule as a gauge origin for the zz-component of the shielding due to the occupied π-MOs. For this gauge the shielding is almost entirely diamagnetic, as required for a free current. In cyclohexatriene this current is somewhat attenuated, as seen from larger paramagnetic contributions. The increased susceptibilities in fulvene and cyclopentadiene are also due to the π-system, though no genuine ring current effects can be detected. In the case of the ^1H shielding a different mechanism is responsible for the deshielding in ethylene (and polyenes) with respect to methane (or paraffins) and for the extra deshielding in benzene relative to ethylene. The latter is due to the occupied π-MOs and related to the ring current. It is calculated to be ~5 ppm in the out-of-plane component, but it is reduced to less than 2 ppm in the isotropic shielding. Ring current effects are not detectable in any other molecules of this study, but in complementary investigations of other Hückel or anti-Hückel annulenes. The ^{13}C shift tensors show a very complicated pattern with large variations already between the isomeric hexatrienes, which are hard to interpret within an increment system. While the shift tensors in fulvene don't differ too much from what one expects for carbon atoms in a similar bonding situation, bis-(methylene)cyclobutene and tris(methylene)cyclopropane are affected by strong ring strain effects. Benzene differs from polyenes mainly in a shielding of the out-of-plane component that is unusually strong for a CH carbon in an unsaturated system. Conclusions on a ring current effect would be premature.

1. Introduction

Molecules with cyclic conjugated π-electron systems have specific magnetic properties, different from those of other π-electron systems. These are, in particular, a stronger diamagnetic susceptibility than expected from additivity rules like those of Pascal,[1] a pronounced anisotropy of the susceptibility, and a deshielding of the protons attached to the ring carbons, as compared to noncyclic conjugated π-systems.

The idea that the "magnetic anomaly" is due to ring currents in the π-electron system is relatively old.[2–5] The first quantum mechanical treatment on the level of Hückel theory[6] has been given by F. London[7] in his famous paper, in which he also introduced the concept of what now is referred to as gauge invariant (or gauge including) orbitals (GIAOs). Soon after the difference in the proton magnetic shielding between benzene and noncyclic olefins was observed,[8] a rationalization in terms of the ring current model was given by Pople,[9] who has also made further contributions to this topic.[10]

The ring current model has been very successful,[11,12] but there have also been critical comments, and some modifications were suggested in the literature.[13–18] The severest criticism was that of J. Musher,[15] who proposed what he called an "antitheory" to that of London, where everything is explained in terms of local quantities. Musher's "antitheory" has also been contested.[11,19] Although most of Musher's claims have meanwhile been regarded as obsolete,[11] has idea to interpret the magnetic properties of benzene and related systems in terms of local quantities has turned out to be useful.[17,18]

The state of affairs around 1980, i.e. before the advent of powerful ab-initio methods for the calculation of magnetic susceptibilities and chemical shifts, has been reviewed by Haigh and Mallion.[11]

† Permanent address: Università Degli Studi di Modena, Dipartimento di Chimica, Via G. Campi 183, I-41100 Modena, Italy.
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We think that it is now time to come to a definite conclusion, since the theoretical methods available should make this possible. We decided to attack the problem from two different sides. On one hand we have performed a comparative theoretical study of the magnetic properties of benzene and some of its isomers as well as some other related molecules, following to some extent a previous investigation by Benson and Flygare,[20] in order to clarify whether the computed properties of benzene need to be explained in terms of a ring current. On the other hand we have done a careful analysis directly of the currents induced in benzene by an external homogeneous magnetic field. We present here the first study, while the second one[21] will be published elsewhere. Let us note that the conclusions drawn so far from current density plots by our two groups were rather different. While the study of Lazzeretti et al.[16,17] suggested reservations against the classical ring current picture, that of Kutzelnigg et al.[22,23] was rather consistent with the ring current model. Of course, these different results were to some extent based on different interpretations of what the London model should imply. The more literally one takes it, the less a confirmation from a rigorous study will result. Anyway, the analysis of the ring currents induced in benzene is far from trivial.

It is, at this point, recommended to distinguish between the original London model of the ring current[7] and a "revised ring current model", in which some of the unjustified assumptions of London are eliminated. These are mainly the claim that σ-electrons don't contribute to the anisotropy and the reference to "superconductivity" of the ring current. Of course, a model is always a simplification of reality, and it can never be entirely correct. Nevertheless, we regard a model as valid if it accounts well for dominant real effects. This will turn out to be the case for the revised ring current model.

In the present paper we shall, after a short presentation of the IGLO method and a description of the used basis sets (section 2), first discuss the magnetic susceptibilities (in particular its different tensor components) of benzene and related compounds (section 3) and then the NMR chemical shifts, namely, for ^{1}H, in section 4 and for ^{13}C in section 5.

The main conclusions of section 3 will be that benzene, fulvene, bis(methylene)cyclobutene, and tris(methylene)cyclopropane differ very little in the *in-plane* components of the susceptibility, while the *out-of-plane* component is exceptionally high for benzene, but for the other isomers much closer to 3 times the value of ethene. The hypothetical cyclohexatriene with alternating single and double bonds is still benzene-like, but halfway to other isomers without cyclic conjugations.

Evidence of the decisive role of the ring current comes from a study of the π-electron system in benzene with the gauge origin in the midpoint of the molecule, which confirms the almost free mobility of the π-system in benzene, while that in cyclohexatriene is less mobile.

In section 4 we shall be concerned with the extra deshielding of the protons in benzene (relative to ethene), which is in agreement with Biot-Savart's law (provided there is a ring current). This effect is much less spectacular than that on the susceptibilities. Nevertheless, a careful analysis confirms that there is a ring current effect on the ^{1}H shielding in benzene, but not in the other isomers. This becomes particularly obvious if one looks at the tensor component perpendicular to the molecular plane.

The interpretation of the results for the ^{13}C shieldings is much more difficult than that of the susceptibilities and the ^{1}H shieldings. In fact even for the polyenes, the shielding tensors vary considerably and are not interpretable by a simple increment system.

2. Method and Basis Sets

The calculations reported here were done by the IGLO method[24-28] (IGLO stands for individual gauge for localized orbitals). This method is of coupled Hartree–Fock (CHF) type with individual gauge origins for different localized orbitals. It has been described in detail elsewhere.[24,25] For a noninitiated reader a recent review[28] is recommended. One of the advantages of the IGLO method (shared by other related methods like LORG[29] or GIAO[30-33]) with respect to the classical CHF with a common gauge origin[34,35] is that one does not have to rely on a cancellation of large spurious diamagnetic and paramagnetic contributions and that the results are not very dependent on the size of the basis, such that acceptable results are obtained even with small or moderate basis sets.

For the present study a very useful feature of IGLO (not shared by GIAO) is that the magnetic properties are obtained as sums of contributions of localized orbitals (inner shells, bonds, lone pairs), which facilitates the interpretation.

The IGLO results for the shieldings (or absolute chemical shifts) σ, or rather for its tensor components σ_{xx}, etc., are obtained as sums of contributions of localized MOs (LMOs). For the susceptibility χ we also get sums of orbital contributions, but in addition a "nonlocal" correction term, which is usually rather small. The standard option is that LMOs according to Boys are used and the gauge origins are taken in the centroids of charge of these. They will in the case of double bonds be banana-like. Alternatively, one can impose a $\sigma-\pi$ separation and get localized σ- and π-bonds. The total results are essentially equivalent, but for χ the nonlocal part χ_{nl} may change. Other choices of the gauge are possible. If one wants to compare results of calculations for different gauges, one must make sure that the basis is large enough such that the overall results don't differ significantly for different gauges. Here, this has been verified (cf. Table 1).

Chemical shifts are obtained in parts per million. We only tabulate absolute shieldings (relative to the bare nucleus), for which the sign convention is such that $\sigma > 0$ means shielding and $\sigma < 0$ deshielding. Susceptibilities χ are displayed in the unit which has exclusively been used so far, namely, in "ppm cgs" or more precisely in 10^{-6} erg G^{-2} mol^{-1} = 10^{-6} cm^3/mol. A conversion to the SI unit is possible (with some reservations, considering the nonuniqueness of magnetic quantities in the SI system) taking 1 ppm cgs = $4\pi \times 10^{-12}$ m^3 mol^{-1}. The conversion factor from atomic units to ppm cgs is 1 au = a_0^3N = 8.9238878×10^{-2} ppm cgs. The sign convention for χ (not always observed in the literature) is such that $\chi < 0$ means diamagnetic and $\chi > 0$ paramagnetism.

All calculations were done with a basis set of "triple-ζ plus polarization" quality ("basis II" following the nomenclature of ref 28). It is constructed from the Huzinaga[36] (9s5p) set for carbon and the (5s) set for hydrogen, contracting it to (51111/2111) and (311) and augmenting it by a d-set for C ($\eta = 1.0$) and a p-set ($\eta = 0.65$) for H.

For benzene we also used a larger basis set to get a near Hartree–Fock limit result. It is constructed from Huzinagas (11s7p) and (6s) for carbon and hydrogen in the contraction (5111111/211111) and (3111) augmented by the following uncontracted sets: (3d1f) and (3p1d), (2.8, 0.7, 0.175; 0.6) and (1.6, 0.4, 0.1; 0.65).

The structural formulas of the considered molecules are shown on Figure 1 together with the numbering of the atoms. These are benzene and its isomers: benzene (**1**), fulvene (**3**), bis(methylene)cyclobutene (**4**), tris(methylene)cyclopropane (**5**), the hypothetical cyclohexatriene with alternating double and single bonds (**2**), cyclopentadiene (**6**), 1,4-cyclohexadiene (**7**), as well as the simple acyclic π-electron systems ethylene (**8**), *s-trans*-butadiene (**9**), *s-cis*-butadiene (**10**), and finally the open and branched hexatrienes **11–18**.

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Table 1. Magnetic Susceptibilities (in ppm cgs, with Sign Reversed)

| molecule | IGLO[a] | | | | | experiment | | | |
	χ_{ip}[b]	χ_{zz}	χ_{av}	$\Delta\chi$	$\delta_{zz}^{inc\ c}$	χ_{ip}[d]	χ_{zz}	χ_{av}	$\Delta\chi$
1a	47.1	109.6	67.9	62.5	42			55.0[e]	
	(46.8	110.2	68.0	63.4)		34.9	94.6		59.7[f]
	37.8[h]	*106.7*	*60.7*	*68.7*		±0.1	±0.1		
	38.7[i]	*107.7*	*61.7*	*69.0*		34.9	94.6	54.8	59.7[g]
	40.0[k]	*108.1*	*62.7*	*68.2*		±2.0	±2.5		
1b	46.7	108.6	67.4	61.8	41				
	(46.5	109.2	67.4	62.7)					
2a	46.3	101.0	64.5	54.7	33				
	(46.2	101.1	64.5	54.9)					
2b	46.1	100.4	64.2	54.3	33				
	(46.1	100.6	64.2	54.6)					
3	44.7	81.0	56.8	36.3	13	30.6	67.6	42.9	37.0[l]
	(44.7	81.1	56.8	36.4)		±1.4	±1.6	±1.0	±0.9
4	45.5	67.4	52.8	22.0	0	29.7	51.3	36.9	21.7[l]
	(45.8	67.5	53.0	21.7)		±6.0	±6.0	±6.0	±0.7
	49.3	78.2	59.0	28.9	12				
	(49.5	78.2	59.0	28.7)					
6	40.8	70.9	50.8	30.1	17				−34.3[l]
	(40.7	71.0	50.8	30.3)					
7	53.0	62.8	56.2	9.8					
	(52.8	63.2	56.3	10.5)					

[a] Values in parenthesis: calculations without σ–π separation in the localization. Entries in italic: other theoretical, near HF-limit data. [b] χ_{ip} = χ_{xx} = χ_{yy} for **1**, **2**, **5**; for **3**, χ_{xx} = 46.3(46.1), χ_{yy} = 43.1(43.3); for **4**, χ_{xx} = 44.6(44.7), χ_{yy} = 46.4(46.8). [c] Deviation of χ_{zz} from the value predicted by the increment system (67.7 for **1**–**5**, 53.9 for **6**). [d] χ_{ip} = χ_{xx} = χ_{yy} for **1**, **2**, **5**; for **3**, χ_{xx} = 30.9 ± 1.2, χ_{yy} = 30.2 ± 1.4; for **4**, χ_{xx} = 29.8 ± 6.0, χ_{yy} = 29 ± 5.0. [e] From ref 5. [f] From ref 43. [g] From ref 44. [h] IGLO with a (11s7p3d1f/6s3p1d) → (7s6p3d1f/4s3p1d) basis. [i] CHF with gauge origin at the center of mass, same basis as *h*. [k] CHF with gauge origin as *i*, from ref 16, best previous theoretical results. [l] From ref 20.

Experimental values for the geometries[37] have been taken for **3**–**7**. For **1** and **8** both experimental and SCF-optimized geometries were used, referred to as **1a**, **1b** and **8a**, **8b**. Two assumed geometries were taken for the hypothetical cyclohexatriene (**2**) with the following geometrical parameters. **2a**: r(C=C) = 1.336 Å, r(C–C) = 1.501 Å, r(C–H) = 1.083 Å, all angles equal to 120°. **2b**: r(C=C) = 1.323 Å, r(C–C) = 1.479 Å, r(C–H) = 1.083 Å, all angles equal to 120°. SCF-optimized geometries were used for **9**–**18**.

3. Magnetic Susceptibilities

The computed and experimental magnetic susceptibilities are collected in Tables 1 and 2. If not indicated otherwise, basis II as described in section 2 has been used. In Tables 1 and 2 we indicate the average χ_{ip} of computed in-plane components χ_{xx} and χ_{yy} as well as the out-of-plane component χ_{zz}, the isotropic part χ_{av}, and the anisotropy Δ_χ defined as

$$\Delta\chi = \chi_{zz} - \chi_{ip}; \quad \chi_{ip} = (1/2)(\chi_{xx} + \chi_{yy}) \qquad (1)$$

If the susceptibilities were simply the sums of bond increments, the molecules **1**–**5** should have the same susceptibilities, which is obviously not the case.

The general experience is confirmed that computed susceptibilities are usually larger in absolute value than the experimental ones, but that with increasing basis size one gets closer to experiment. For benzene an IGLO calculation with a much larger basis (described in section 2) is included in Table 1. The isotropic part, χ_{av} = 60.7 ppm cgs, is slightly less than the best theoretical value published so far[16] and is supposed to be close to the Hartree–Fock limit. It is still somewhat larger than the experimental value (55 ppm cgs). The remaining difference is probably due to correlation effects.

Since the deviations between theoretical and experimental results are rather systematic, we can base the following qualitative discussion on the computed basis II IGLO results. The first

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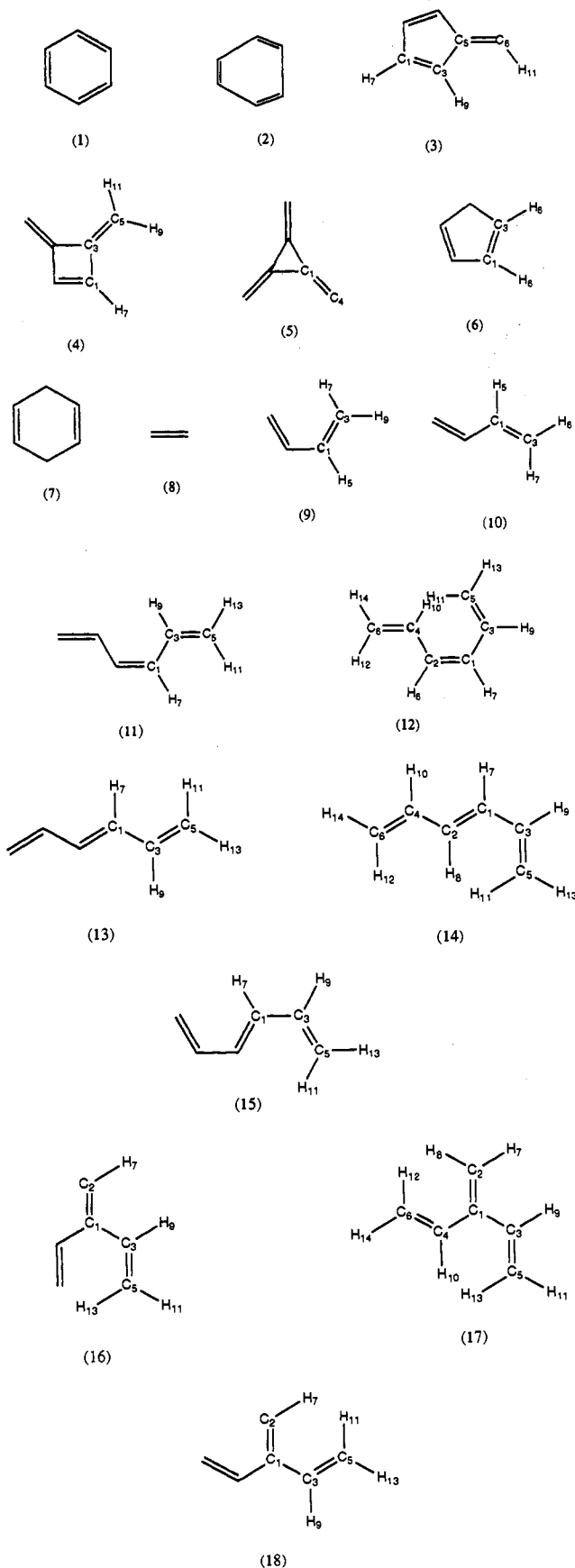
Figure 1. Structural formulas and numbering of atoms for the molecules studied.

remarkable observation is that χ_{ip} is, within a few ppm cgs, the same for all benzene isomers and nearly indistinguishable from that of cyclohexatriene. However χ_{zz} differs considerably in these

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Table 2. Calculated Magnetic Susceptibilities (in ppm cgs, with Sign Reversed)

	$\chi_{ip}{}^a$	$\chi_{zz}{}^b$	$\chi_{zz}(\pi)^c$	nl^d	$\chi_{av}{}^e$
8a	19.9	27.7	6.19	0.04	22.5^f
8b	20.0	27.4	6.07	-0.07	22.5^f
9	35.0	48.6	5.99	-2.42	39.5
10	35.1	51.3	6.48	-0.21	40.5
11	50.0	75.1	6.85	-1.17	58.4
12	50.1	70.6	6.87	-4.17	57.0
13	49.9	75.5	6.80	-0.56	58.5
14	49.7	72.3	6.53	-3.36	57.3
15	49.6	69.4	5.96	-5.06	56.2
16	49.8	72.4	6.66	-1.83	57.3
17	49.7	74.8	6.26	-1.47	58.0
18	49.6	72.0	5.95	-3.44	57.1

^{a} Average of the χ_{xx} and χ_{yy} components. ^{b} Component perpendicular to the molecular plane. ^{c} Average contribution of one π-MO to χ_{zz}. ^{d} Nonlocal contributions. ^{e} Isotropic value. ^{f} 19.7 from ref 45, 18.8 ± 0.8 from ref 46.

compounds, with $|\chi_{zz}|$ in benzene significantly higher than for all other isomers.

From the data of ethylene, butadiene, and hexatriene (obtained with the same basis) one can derive IGLO increments separately for χ_{ip} and χ_{zz} for an ethylene unit and the difference of the increments of two CH bonds and one CC single (sp²) bond, namely (for the derivation see the appendix),

$$\chi_{ip}(C_2H_4) \approx -20.0 \text{ ppm cgs}$$

$$2\chi_{ip}(CH) - \chi_{ip}(C-C) \approx -5.0 \text{ ppm cgs}$$

$$\chi_{zz}(C_2H_4) \approx -27.4 \text{ ppm cgs}$$

$$2\chi_{zz}(CH) - \chi_{zz}(C-C) \approx -4.9 \text{ ppm cgs}$$

From this increment system one predicts for benzene and all of its isomers

$$\chi_{ip}(C_6H_6) \approx -45.1 \text{ ppm cgs}$$

$$\chi_{zz}(C_6H_6) \approx -67.7 \text{ ppm cgs}$$

In all benzene isomers χ_{ip} agrees roughly with the estimate for nonconjugated (or polyene-like conjugated) double bonds, while χ_{zz} is in agreement with this prediction only for bis(methylene)-cyclobutene. $|\chi_{zz}|$ is larger by ~10-15 ppm cgs for fulvene and tris(methylene)cyclopropane and larger by 42 ppm for benzene. In the hypothetical cyclohexatriene $|\chi_{zz}|$ is still 33 ppm larger than for a molecule with isolated double bonds.

Note that there is an anisotropy of ca. -23 ppm even "in the absence of any ring current", i.e. assuming additive increments. The anisotropy is not entirely due to the ring current (as assumed originally by London[7]).

Benson and Flygare[20] have, on the basis of their data, derived an increment system for $\Delta\chi$ and conclude that from their system $\Delta\chi$ for all benzene isomers predicted by the system should be -26 ppm cgs. In view of the different definition of the increment systems the agreement with the conclusions from our system is satisfactory.

Long ago Dauben et al. suggested to take the exaltation of the (absolute value of the) isotropic susceptibility as a measure of aromaticity.[38] Since χ_{ip} does not differ significantly from the predictions by an increment system, $|\chi|$ should be enhanced by roughly one-third of the enhancement of $|\chi_{zz}|$. The exaltation of 13.7 ppm cgs given by Dauben et al. is very close to one-third of our $|\chi_{zz}|$ enhancement. In view of their smaller magnitude, exaltations of $|\chi|$ are less easily detected than those of $|\chi_{zz}|$.

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Table 3. Contributions to χ_{zz} (in ppm cgs, with Sign Reversed)

molecule	$\pi_1{}^a$	$\pi_2{}^a$	$\pi_3{}^a$	π^b	nl^c	σ^d	tot^e	x^f
1a	16.98	16.98	16.98	50.94	7.62	51.58	109.60	43.1
1b	16.76	16.76	16.76	50.28	7.37	50.92	108.57	42.2
2a	13.93	13.93	13.93	41.79	7.76	51.40	100.95	34.1
2b	13.95	13.95	13.95	41.85	7.42	51.40	100.43	33.8
3	7.56	7.56	8.12	23.24	4.75	53.04	81.03	12.5
4	7.44	6.59	6.59	20.62	-3.39	50.18	67.41	1.8
5	7.50	7.50	7.50	22.50	-1.88	57.60	78.22	5.1
6	8.21	8.21	4.73^g	16.42	4.79	49.60	70.85	10.9
7	5.13	5.13	3.43^g	10.26	-5.77	58.27	69.76	-5.8

^{a} Contribution of a single π-bond. ^{b} Sum of the π-contributions. ^{c} Nonlocal contributions. ^{d} σ-contribution. ^{e} Total χ_{zz}. ^{f} π + nl minus 3 times the difference of butadiene and ethylene (5.16) (for **6** and **7** minus 2 times the latter). ^{g} Contribution of the π-like MO of the CH_2 group, not included in the sum (π); there are two of these in **7**.

What one cannot do in experiment, but in an IGLO calculation, is to decompose χ into σ- and π-contributions. The results are given in Table 3. The σ-contribution to χ_{zz} is practically the same in all C_6H_6 isomers, while both the π-contribution and the nonlocal part differ greatly. Note that "nonlocal" has a different meaning in our context (see section 2) and in ref 20, where this term is used for the excess over the results predicted from an increment system.

There is some indication (see later) to take the π-contribution plus the nonlocal terms as some "effective" π-contribution. The analogous contribution in ethylene is 6.23 ppm cgs; for 3 times ethylene one hence expects an effective π-contribution of 18.69 ppm cgs. The effective π-contributions in **4** and **5** differ by less than 2 ppm cgs from this (see x in Table 3). We conclude that in **4**—see also Table 1—there is no enhanced π-contribution to $|\chi_{zz}|$, hence no detectable ring current effect. The increase of $|\chi_{zz}|$ by about 10 ppm cgs in tris(methylene)cyclopropane (**5**) comes from a σ-contribution, probably a ring strain effect, hence no ring current effect in **5** either.

The enhancements of the π-contribution to $|\chi_{zz}|$ in benzene (**1**), cyclohexatriene (**2**), and fulvene (**3**)—displayed in Table 3—are in rough agreement with the enhancements (Table 1) according to our increment system.

The various isomeric open-chain and branched hexatrienes (Table 2) show some variation in χ_{zz}, while χ_{ip} is practically the same in all isomers. The variations of χ_{ip} by a few ppm cgs appear to be due to variations in the nonlocal contributions to χ, not to differences in the π-contributions. They are hence no indication of differences in π-conjugation.

Now we can perform another computer experiment to pinpoint the ring current effect in benzene. If there were an *ideal ring current* in the π-system in benzene, this would mean that the π-MOs were eigenfunctions of the angular momentum operator l_z along the 6-fold molecular axis. This would then have the consequence that with respect to a *gauge origin at the midpoint of the molecule* the π-contribution to χ_{zz} would consist of a diamagnetic part only. We find (see Table 4) that for this gauge the π-contribution to χ_{zz} is ca. -60 ppm cgs, with a paramagnetic part of only ~4.5 ppm. The total π-contribution to χ_{zz} consists of ca. -17.10 ppm cgs for the a_{1u} MO and ca. -19.05 ppm cgs for either of the e_{1u} MOs. One notes the closeness of these values. For an ideal ring current of radius 2.46 a_0 (the actual radius of benzene) one would expect ca. -51 ppm cgs, in good agreement with an old estimate of Pauling on the same line.[4] There could hardly be a better confirmation of the (revised) ring current model for benzene (for the definition of the revised ring current model see the Introduction).

In a standard IGLO approach with gauge origins in the centroids of charge of the respective π-type LMOs (localized molecular orbitals) one gets a diamagnetic contribution to χ of ca. -12 ppm cgs and a (total) paramagnetic contribution of ca. -5 ppm cgs for each π-bond. The assumptions that the LMOs are approximate eigenfunctions of a local angular momentum operator are much less satisfied than for a common gauge at the

Table 4. Contributions[a] to χ_{zz} (in ppm cgs, with Sign Reversed) for Benzene and Cyclohexatriene Using Two Different Localization Schemes (for the π-MOs)

	type[a]	π_1	π_2	π_3
1a	d	18.11	20.82	20.82
πs canonical	p	−1.01	−1.77	−1.77
	χ	17.10	19.05	19.05
	nl		2.18	
1b	d	17.82	20.53	20.53
πs canonical	p	−0.97	−1.70	−1.70
	χ	16.85	18.22	18.22
	nl		1.99	
2a	d	18.27	20.41	20.41
πs canonical	p	−1.34	−4.99	−4.73
	χ	16.92	15.42	15.68
	nl		2.17	
2b	d	18.71	20.78	20.78
πs canonical	p	−1.45	−5.48	−5.19
	χ	17.26	15.30	15.59
	nl		2.52	
1a	d	12.20	12.20	12.20
πs localized	p	4.78	4.78	4.78
	χ	16.98	16.98	16.98
	nl		7.62	
1b	d	12.03	12.03	12.03
πs localized	p	4.73	4.73	4.73
	χ	16.76	16.76	16.76
	nl		7.37	
2a	d	9.52	9.52	9.52
πs localized	p	4.43	4.43	4.43
	χ	13.95	13.95	13.95
	nl		7.42	
2b	d	9.56	9.56	9.56
πs localized	p	4.37	4.37	4.37
	χ	13.93	13.93	13.93
	nl		7.56	

[a] d, diamagnetic contribution for one π-MO; p, paramagnetic contribution for one π-MO; nl, sum of nonlocal contributions; χ, total contributions of one π-bond.

center of the molecule. For this distributed gauge one has moreover a rather large nonlocal contribution to χ_{zz} of ~8 ppm cgs, while the nonlocal contribution is only ~2 ppm cgs for the common gauge at the molecular center.

This observation—which indicates that the common gauge at the center of the molecules is more physical (in the sense that spurious paramagnetic contributions are as small as possible) than IGLO type distributed gauge origins and confirms the validity of the ring current model—is, of course, limited to the π-contribution to χ_{zz}. Already, for the π-contribution to $\chi_{xx} = \chi_{yy}$ the distributed gauge origin is definitely superior to a common gauge origin, as is seen from the magnitude of the paramagnetic contributions (not documented here). The same is true for all components of the contributions of the σ-electrons.

Let us now compare benzene with cyclohexatriene for the same gauge (see Table 4). There is rather little change in the diamagnetic π-contributions to χ_{zz} as compared to benzene. However, the paramagnetic contributions are definitely larger in magnitude, namely, a total of ~12 ppm cgs, compared to only ~5 ppm cgs for benzene. This indicates that the assumption of a freely rotating π-stream, for MOs that are eigenfunctions of l_z along the 6- or 3-fold molecular axis, is much less justified. By distorting **1** to **2**, we obviously destroy the ring current partially, and we get a total reduction of the π-contribution to χ_{zz} by ~6 ppm, which accounts for the bulk of the difference between **1** and **2**.

Since the total π-contribution is not invariant with respect to the change of gauge just discussed, we can compare a fully localized calculation and a calculation with the appropriate gauge for the π-ring current only if we take care of the difference of 6 ppm between the nonlocal contributions.

The exceptional role of benzene is obvious. Nevertheless, our results are not inconsistent with the idea that there is some ring current (though much weaker than in benzene) even in fulvene.

This is in at least qualitative agreement with the Hückel resonance energies of the benzene isomers. If we measure these relative to hexatriene, then **1** has the resonance energy 1β, **3** has 0.5β, **4** has 0.2β, and **5** 0.3β. It is, however, generally believed that the HMO resonance greatly overestimates the delocalization for the benzene isomers.

While the enhancement of $|\chi_{zz}|$ with respect to the prediction from an increment system in fulvene (**3**) is without doubt (in agreement with the findings of Benson and Flygare[20]), going from $|\chi_{zz}|$ to $|\chi|$ the enhancement of 13 ppm cgs is reduced by one-third i.e. to about 4 ppm cgs. Dauben et al.[38] found only 1 ppm cgs and concluded that there is no significant exaltation. This is another indication that the isotropic susceptibility is less sensitive to ring current effects than is $|\chi_{zz}|$.

One of the most puzzling results of Benson and Flygare[20] was that cyclopentadiene (**6**) has a very large anisotropy of χ_{zz}, much higher than that in *cis*-butadiene and very comparable to that in the aromatic system furane, though smaller than in pyrrole, thiophene, or the cyclopentadienyl anion. To analyze the results for cyclopentadiene, we need first to estimate what one should get from an increment system. This is possible using results for 1,4-cyclohexadiene as outlined in the Appendix. One finds that $|\chi_{zz}|$ in cyclopentadiene is larger by ~17 ppm cgs than predicted by the increment system. Qualitatively, this agrees with the finding of Benson and Flygare, indicating that there is a nonnegligible hyperconjugative effect as far as the susceptibility of cyclopentadiene is concerned. This is in contrast to a lack of any thermochemical evidence for hyperconjugation in cyclopentadiene.[39]

Cyclopentadiene is also included in Tables 1 and 3. Although a direct comparison with the genuine six π-electron systems is not possible, the enhancement of the π-contributions—especially if one compares it with 1,4-cyclohexadiene—is consistent with the picture of some hyperconjugation. The enhancement of 17 ppm cgs for **6** (with 0 per definition for **7**) corresponds to an enhanced π-contribution of 10.9 for **6** and −5.8 for **7** in Table 3.

Again we can have a look at the exaltation of the isotropic susceptibility $|\chi|$ as advocated as an aromaticity criterion by Dauben et al.[38] One-third of 17 ppm cgs is ~6 ppm cgs, in good agreement with the 6.5 found by Dauben et al., which they hesitated, however, to regard as significant.

4. Proton Shieldings

In Tables 5 and 6 ^{1}H shielding tensors are displayed. A comparison with experimental results, whenever they are available, is given in Tables 6 and 7. The agreement is usually quite good.

While the effect of the ring current on the susceptibility of benzene is spectacular and hard to miss, the effect on the ^{1}H shielding is much more subtle and not so easy to detect. Chemical shifts mainly monitor local effects and to a much lesser extent global ones (like ring currents). This is due to the dependence of the relevant operators on some inverse powers of the distance to the nucleus. The proton shielding is mainly determined by the LMO of the CH bond, which is not so different in different environments. The difference between a proton attached to a CC single or double bond is already a non-nearest-neighbor effect and rather small. A CC double bond creates a deshielding of the proton of ~5 ppm that must be discriminated from the extra deshielding of ~2 ppm in benzene, supposedly due to the ring current. According to Biot-Savart's law, a diamagnetic (shielding) current creates a field opposed to the applied one inside the ring (which is responsible for the increased diamagnetism) but a field parallel to the applied one outside the ring, thus deshielding the protons in benzene.

A discrimination of the two deshieldings is possible due to their different mechanism. The "olefin deshielding" is related to the existence of a low-lying π*-MO, which causes local paramagnetic currents around axes in the molecular plane.

(39) Roth, W. (Bochum) private communication.

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Table 5. Contributions to the ^{1}H Shielding (in ppm)[a]

molecule	bond	σ_{33}	σ_{22}	σ_{11}	σ_{av}
CH$_4$	CH	29.27	23.00	23.00	25.09
	total	38.23	27.48	27.48	31.07
C$_2$H$_6$	CH	28.84	24.08	23.87	25.60
	total	37.28	27.58	26.08	30.45
C$_2$H$_4$ (8a)	CH	26.99	23.20	27.88	26.02
	CH'	−3.93	2.33	1.20	−0.14
	CC-σ	1.03	1.01	−8.54	−2.16
	CC-π	4.85	−0.02	2.77	2.53
	total	29.65	25.36	22.55	25.85
(8b)	CH	27.29	23.34	27.81	26.14
	CH'	−4.13	2.33	1.33	−0.16
	CC-σ	0.96	1.04	−8.08	−2.03
	CC-π	4.90	−0.03	2.98	2.62
	total	29.77	25.47	23.28	26.17
C$_6$H$_6$ (1a)	CH	24.94	29.39	23.32	25.88
	π	5.35	4.46	−3.17	2.21
	total	26.41	25.96	20.24	24.20
(1b)	CH	25.07	29.56	23.46	26.03
	π	5.41	4.62	−3.16	2.29
	total	26.61	26.31	20.36	24.43
C$_6$H$_6$ (2a)	CH	26.13	28.25	23.30	25.89
	π	4.84	4.59	−2.58	2.29
	total	26.99	25.26	20.90	24.38
(2b)	CH	27.92	26.53	23.36	25.94
	π	4.80	4.90	−2.65	2.35
	total	27.15	25.70	20.84	24.56

[a] The orientation of the principal axes is sketched in Figure 2; it should be noted that σ_{zz} is σ_{11} in **1** and **2**, whereas it is σ_{22} in **8**.

Table 6. Principal Values of the Computed Hydrogen Shielding Tensors (in ppm) (Components Perpendicular to the Molecular Plane in Boldface)

molecule	atom	type	σ_{33}	σ_{22}	σ_{11}	σ_{av}	$\sigma_{zz}(\pi)$
1a		CH	26.4[a]	25.9[a]	**20.1**[a]	24.1	−3.17
1b		CH	26.7[a]	26.3[a]	**20.4**[a]	24.4	−3.16
2a		CH	27.0	25.3	**20.9**	24.4	−2.58
2b		CH	27.2	25.7	**20.8**	24.6	−2.65
3	H$_7$	CH	27.7	23.4	**23.4**	24.9	−0.67
	H$_9$	CH	27.8	24.1	**23.3**	25.1	−0.92
	H$_{11}$	CH$_2$	29.3	23.3	**22.6**	25.1	−1.02
4	H$_7$	CH	26.4	**23.4**	21.4	23.8	−0.99
	H$_9$	CH$_2$	30.8	25.4	**24.7**	26.9	−0.30
	H$_{11}$	CH$_2$	30.2	25.7	**24.7**	26.9	0.06
5		CH$_2$	29.3	25.3	**22.6**	25.7	−0.63
6	H$_6$	CH	28.5	23.3	**23.1**	25.0	−1.13
	H$_8$	CH	27.1	24.8	**23.5**	25.1	−0.64
7	H$_7$	CH	29.3	24.9	**23.7**	26.0	0.35
8a		CH$_2$	29.7[a]	**25.4**[a]	22.6[a]	25.9	−0.02
8b		CH$_2$	29.8[a]	**25.5**[a]	23.3[a]	26.2	−0.03
9	H$_5$	CH	29.2	24.6	**24.5**	26.1	0.86
	H$_7$	CH$_2$	29.9	24.0	**23.9**	26.0	−0.91
	H$_9$	CH$_2$	30.2	24.6	24.2	26.3	−0.39
10	H$_5$	CH	29.4	**24.1**	23.1	25.5	−0.26
	H$_7$	CH$_2$	30.4	**25.0**	23.7	26.4	−0.47
	H$_8$	CH$_2$	30.2	**25.0**	24.0	26.4	−0.04
11	H$_7$	CH	29.9	24.4	**23.6**	26.0	−0.20
	H$_9$	CH	30.4	**22.7**	22.7	25.2	−0.33
	H$_{11}$	CH$_2$	30.5	**24.7**	23.6	26.3	−0.60
	H$_{13}$	CH$_2$	30.5	**24.6**	23.9	26.3	−0.28
13	H$_7$	CH	30.2	**23.7**	22.9	25.6	−0.65
	H$_9$	CH	29.6	**23.9**	23.4	25.6	−0.12
	H$_{11}$	CH$_2$	30.6	**24.7**	23.7	26.3	−0.54
	H$_{13}$	CH$_2$	30.4	**24.8**	23.9	26.3	−0.19
16	H$_7$	CH$_2$	30.6	**24.4**	23.6	26.2	−0.61
	H$_9$	CH	30.4	23.8	**23.2**	25.8	−0.14
	H$_{11}$	CH$_2$	30.2	25.0	**24.6**	26.6	−0.13
	H$_{13}$	CH$_2$	30.2	25.4	**22.9**	26.2	−0.41

[a] Experimental data from ref 47, relative to the isotropic shieldings: (1) 1.8, 1.8, −3.5; (8) 2.5, −0.9, −1.6; to be compared to (1a) 2.3, 1.8, −4.0; (1b) 2.3, 1.9, −4.0; (8a) 3.8, −0.5, −3.3; (8b) 3.6, −0.7, −2.9.

Table 7. Hydrogen Chemical Shifts (in ppm)[a]

molecule	atom	IGLO	experiment
1a		7.0	7.27[b]
1b		6.7	
3	H$_7$	6.1	6.53,[c] 6.44[b]
	H$_9$	6.0	6.22,[c] 6.11[b]
	H$_{11}$	6.0	5.85,[c] 5.78[b]
4	H$_7$	7.3	6.84[d]
	H$_9$	4.1	4.59[d]
	H$_{11}$	4.2	4.70[d]
5		5.4	5.14,[e] 5.02[f]
6	H$_6$	6.1	6.43[b]
	H$_8$	5.9	6.28[b]
7	H$_7$	5.1	5.70[b]
8a		5.2	5.31,[g] 5.29[b]
8b		4.9	
10	H$_5$	5.5	6.26[b]
	H$_7$	4.7	5.16[b]
	H$_8$	4.6	5.05[b]

[a] With respect to TMS; the calculated shielding σ_H(TMS) is 31.0. [b] Reference 48. [c] Reference 49. [d] Reference 50. [e] Reference 51. [f] Reference 52. [g] Reference 53.

contribution is that of the CH bond, which amounts to 25.09 ppm, while any of three CH' bonds contributes 1.99 ppm.[26,28]
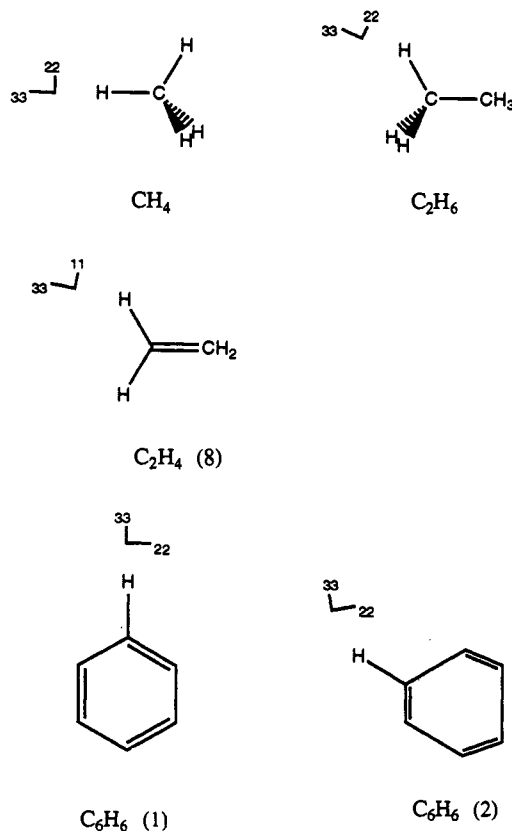
For a comparison with ethylene and benzene we must look separately at the components $\sigma_\parallel$ and σ_{ip} in the direction of the CH bond and perpendicular to it. We find for $\sigma_\parallel$ a contribution of 29.27 ppm of the CH bond in which H is involved, a contribution of 8.96 of the three other CH' bonds, and a total $\sigma_\parallel = 38.23$ ppm. The corresponding contributions to σ_{ip} are 23.00 and 4.48 ppm, with a total $\sigma_{ip} = 27.48$. The replacement of one CH by a CC bond in C$_2$H$_6$ changes relatively little.

In ethylene we get the isotropic shielding of 25.73 ppm, i.e. a deshielding with respect to CH$_4$ of 5.34 ppm. The contribution of the π-bond to the isotropic shielding σ(H) in C$_2$H$_4$ is +2.54 ppm.

Now we have to consider the three tensor components of σ(H). Unfortunately, the principal axis system in C$_2$H$_4$ is different from that in CH$_4$ (and C$_6$H$_6$) insofar as in C$_2$H$_4$ no principal axis agrees with the CH bond direction. Only the z-axis is a principal axis in all systems. For ethylene we get $\sigma_{zz} = 25.35$ ppm, consisting of a CH bond contribution of 23.32 ppm and a contribution of 2.03 ppm of the other two bonds (including a π-contribution of −0.02 ppm). There is relatively little change to the corresponding component in CH$_4$ or C$_2$H$_6$. The sum of the two other tensor components is significantly reduced from 65.71 in CH$_4$ to 51.74 ppm in ethylene. The dominating effect for the deshielding in C$_2$H$_4$ relative to CH$_4$ or C$_2$H$_6$ comes from in-plane (i.e. σ) MOs, in particular from a contribution of −8.76 ppm of the CC-σ-bond, which can be rotated to the antibonding π^*-MO. We note that there is practically *no* contribution of the π-MO to σ_{zz}, only to σ_{xx} and σ_{yy}, where there is a shielding of 2.8 or 4.8 ppm.

The tensor components of σ(H) are changed rather little on going from ethylene to the butadienes or the hexatrienes. σ_{zz} varies between 23.9 and 25.4, while the two in-plane components vary between 28.7 and 30.2 or 22.5 and 24.4 ppm, respectively. The corresponding values for the benzene isomers are hardly outside the same ranges, but benzene differs definitely isofar as σ_{zz} is only 20.1 ppm; that is, there is a reduction of ∼5 ppm with respect to systems with nonconjugated (or polyene-like conjugated) double bonds. If we now look at the LMO contributions to σ_{zz} in benzene, we find a π-contribution of −3.17 ppm. This is obviously responsible for the bulk of the extra deshielding in benzene. This π-contribution is reduced to −2.58 ppm in cyclohexatriene. This is consistent with the reduced ring current.

On going from genuine olefins to benzene or cyclohexatriene not only σ_{zz}(H) is changed but also the two in-plane components to σ(H). However, the sum of these two components remains almost invariant. In view of the different orientations of the principal axis system in benzene and olefins (see Figure 2) the sum of the two in-plane principal values is probably more

An analysis of the contributions to the proton chemical shift in ethylene, together with that in methane and ethane, is given in Table 5. The situation is relatively complicated. In CH$_4$ one computes an isotropic σ(H) of 31.07 ppm. The dominating

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Figure 2. Orientation of the principal axes of the hydrogen shielding tensors in CH₄, C₂H₆, **8**, **1**, and **2**.

meaningful than these values separately. The extra deshielding of the protons in benzene is manifest in the σ_{zz} component; it levels out somewhat if one considers the isotropic shielding, where the effect is less than 2 ppm. Curiously enough, a very similar $\sigma(\text{H})$ as in benzene is found for the ring proton in bis(methylene)-cyclobutene, which is the least expected compound to display ring current behavior. Actually, the low $\sigma(\text{H})$ in **4** is due to a low *in-plane* component, probably related to a ring strain effect, and no indication at all of a ring current.

If there were, as suggested by the susceptibility results, a ring current in **3**—or in **6**—of less than a third the "intensity" as in benzene, an extra deshielding of the ring protons of 1 ppm for $\sigma_{zz}(\text{H})$ and much less than 1 ppm for $\sigma_{av}(\text{H})$ might be expected. Unfortunately, the data in Tables 5 and 6 don't allow any definite conclusion. Although in **3** and **6** there are reduced out-of-plane components of $\sigma(\text{H})$, obviously due to a deshielding of the π-system of ~ 1 ppm for any of the three protons, similar deshieldings are also found in **4** or **5** and even for one of the protons in butadiene **10** and other open-chain π-systems.

The only molecule in this study for which the unusual ¹H shielding is definitely an indication of a ring current effect is benzene.

The conclusions reached on the ring current effect on $\sigma(\text{H})$ in benzene are supported by two complementary IGLO studies. Firstly, it has been found[22,40] that $\sigma_{zz}(\text{H})$ in idealized Hückel annulenes depends nearly linearly on both the effective charge and the number of π-electrons. On going from $n = 2$ to $n = 6$ and $n = 10$ for the same charge, one finds changes of $\sigma_{zz}(\text{H})$ of about 7 ppm. Secondly, by means of the MC-IGLO method,[41] it has been possible to study cyclobutadiene even in its square geometry. As an anti-Hückel system, it has a strong paramagnetic ring current in the π-system and consequently a reduced χ_{zz} and an increased $\sigma_{zz}(\text{H})$ with respect to the case of independent π-systems.

(40) Fleischer, U. To be published.

Table 8. Principal Values of the Computed Carbon Shielding Tensors

molecule	atom	$\sigma_{33}(zz)$	σ_{22}	σ_{11}	σ_{av}
1a		191.7[a]	49.8[a]	−60.3[a]	60.4
1b		193.6[a]	52.8[a]	−56.1[a]	63.4
2a		186.5	56.5	−61.7	60.4
2b		188.3	59.7	−56.1	64.0
3	C₁	161.6	70.9	−68.8	54.6
	C₃	162.9	87.1	−62.2	62.6
	C₅	155.9	48.6	−82.4	40.7
	C₆	168.3	67.3	−48.6	62.3
4	C₁	157.1	45.8	−96.5	35.5
	C₃	145.4	55.4	−80.9	40.0
	C₅	185.7	111.2	−7.5	96.4
5	C₁	212.4	45.9	−51.6	68.9
	C₄	184.0	88.3	−5.4	89.0
6	C₁	161.3	75.8	−69.1	56.0
	C₃	169.5	64.8	−73.7	53.6
7		174.5	85.5	−78.8	60.4
8a		182.5[a]	88.0[a]	−82.9[a]	62.6
8b		184.0[a]	90.3[a]	−71.2[a]	67.7
9	C₁	175.0	79.6	−74.7	60.0
	C₃	186.3	102.2	−52.8	78.5
10	C₁	164.9	72.7	−78.2	53.1
	C₃	175.5	98.6	−50.0	74.7
11	C₁	160.6	79.9	−53.8	62.2
	C₃	180.9	72.2	−77.0	58.7
	C₅	174.3	97.1	−49.6	73.9
12	C₁	171.4	85.9	−47.5	69.9
	C₂	157.0	78.9	−57.5	59.5
	C₃	172.1	78.1	−73.9	58.8
	C₄	179.3	70.1	−77.2	57.4
	C₅	178.0	91.5	−46.7	73.3
	C₆	172.9	93.7	−54.5	70.7
13	C₁	156.0	76.3	−57.0	58.4
	C₃	166.6	72.3	−77.2	53.9
	C₅	175.2	99.4	−50.1	74.8
14	C₁	165.3	84.6	−54.1	65.3
	C₂	167.7	78.7	−59.8	62.2
	C₃	175.4	78.2	−74.7	59.6
	C₄	165.4	72.0	−77.3	53.4
	C₅	185.0	102.3	−50.4	78.8
	C₆	175.0	99.4	−48.8	75.2
15	C₁	178.0	88.4	−57.4	69.7
	C₃	175.3	79.0	−74.5	59.9
	C₅	185.6	102.7	−50.9	79.1
16	C₁	179.0	51.9	−84.2	48.9
	C₂	154.4	90.1	−52.5	64.0
	C₃	155.0	79.8	−74.4	53.4
	C₅	180.9	94.5	−40.9	78.1
17	C₁	177.1	59.8	−79.1	52.6
	C₂	173.8	102.7	−41.6	78.3
	C₃	157.2	76.6	−77.8	52.0
	C₄	181.9	81.0	−74.2	62.9
	C₅	185.4	99.4	−41.8	81.0
	C₆	184.8	101.6	−50.8	78.5
18	C₁	174.4	67.1	−77.4	54.7
	C₂	189.6	111.2	−40.2	86.9
	C₃	158.2	80.9	−75.3	54.6
	C₅	184.9	103.2	−50.7	79.1

[a] Experimental data from ref 47, relative to the isotropic shieldings: (**1**) (three different sets of experimental data are given in ref 47) 119, −21, −97; 121, −16, −104; 120, −60, −60; (**8**) 102, 6, −108; to be compared to (**1a**) 131.3, −10.6, −120.7; (**1b**) 130.2, −10.6, −119.5; (**8a**) 119.9, 25.4, −145.5; (**8b**) 116.3, 22.6, −138.9.

5. Carbon Shieldings

The ¹³C shieldings show a very large variation in the studied compounds; moreover, all $\sigma(\text{C})$ tensors are highly anisotropic, with σ_{zz} roughly 175 ppm and the two in-plane components roughly +85 and −65 ppm, but with variations of about ±25 ppm. The IGLO calculations are listed in Table 8 and compared with experimental data in Tables 8 and 9.

From the ring current picture and Biot-Savart's law one shoud expect *no* ring current effect on $\sigma(\text{C})$, not even in benzene, because the C atoms are neither inside nor outside the ring current. Only for extracyclic carbon atoms like in fulvene a deshielding due to a ring current might be possible. One would, however, expect

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Table 9. Carbon Chemical Shifts (in ppm)[a]

molecule	atom	IGLO	experiment
1a		132.4	128.5[b]
1b		129.3	
3	C_1	138.1	134.3[b]
	C_3	130.1	124.9[b]
	C_5	152.0	152.6[b]
	C_6	130.4	123.4[b]
4	C_1	157.2	145.8[c]
	C_3	152.8	149.7[c]
	C_5	96.3	94.5[c]
6	C_1	136.7	132.2[b]
	C_3	139.1	132.8[b]
7		132.3	125.5[b]
8a		130.1	123.5[b]
8b		125.0	
10	C_1	139.6	137.2[d]
	C_3	118.0	116.6[d]

[a] With respect to TMS; the calculated shielding σ_C(TMS) is 192.7. [b] Reference 54. [c] Reference 55. [d] Reference 56.

Table 10. Typical Principal Values of Carbon Shielding Tensors for Different Bonding Situations in Polyenes[a]

type[b]		$\sigma_{33}(zz)$	σ_{22}	σ_{11}	σ_{av}
1	CH_2	183.3	89.2	−77.1	65.2
		0.7	1.2	5.8	2.6
2	CH_2	180.3	98.9	−49.1	76.6
		7.4	7.4	8.2	5.9
3	CH_2	172.6	101.3	−43.3	76.3
		18.2	11.2	8.6	12.3
4	CHR	172.8	75.0	−76.1	57.2
		8.1	4.9	2.2	3.8
5	CHR	165.2	81.8	−55.3	63.9
		12.8	5.5	7.8	6.0
6	CHR	163.1	79.6	−75.4	55.7
		18.8	3.0	2.4	7.2
7	CR_2	176.8	59.6	−80.2	52.1
		2.4	7.7	4.0	3.2

[a] Average values of the systems studied belonging to each type and maximum deviations (in absolute value) are given in consecutive lines. [b] See Figure 3.

that it is independent of the nucleus, i.e. on the order of only a few parts per million which is so small on the carbon scale that it will, if it exists, certainly be hidden by local effects.

Since, as mentioned before, chemical shifts mainly monitor local effects, we should try to explain the large variations of the ^{13}C shifts between the benzene isomers in terms of local properties, if we want to claim that all isomers except benzene itself consist essentially of isolated double bonds.

One sees from Table 8 that the shielding tensors vary a lot even for the noncyclic conjugated molecules **8–18**. On closer inspection one sees that σ(C) depends (a) on whether the C-atom bears two, one, or no hydrogens and (b) on whether the neighboring C-atom(s) is of this type (are of these types). There are, of course, additional factors influencing the tensor components, e.g. whether a distant C=C bond is cis or trans with respect to the C=C bond in which the considered C-atom is involved.

In ref 26 an increment system for the isotropic σ(C) has been derived from IGLO data. This concept can probably be generalized to the tensor components, although with a little more difficulty and less precision, since the scatter of the data is larger than for the isotropic values. We have not attempted to build up an increment system and rather give in Table 10 typical tensor components for the bonding situations illustrated in Figure 3.

In Table 11 the actual data for the C_6H_6 isomers (and for C_1 of **6**) are compared to those of the corresponding types.

One sees from Table 11 that the most shielded component, σ_{33}, shows the least scatter for polyenes as well as for the cyclic systems. The largest deviations from the polyene values arise (not unexpectedly) for the three-membered ring (**5**) and to some extent for the four-membered ring (**4**). Benzene has the second highest shielding (after **5**). Its σ_{33} lies 16 ppm above the average of all
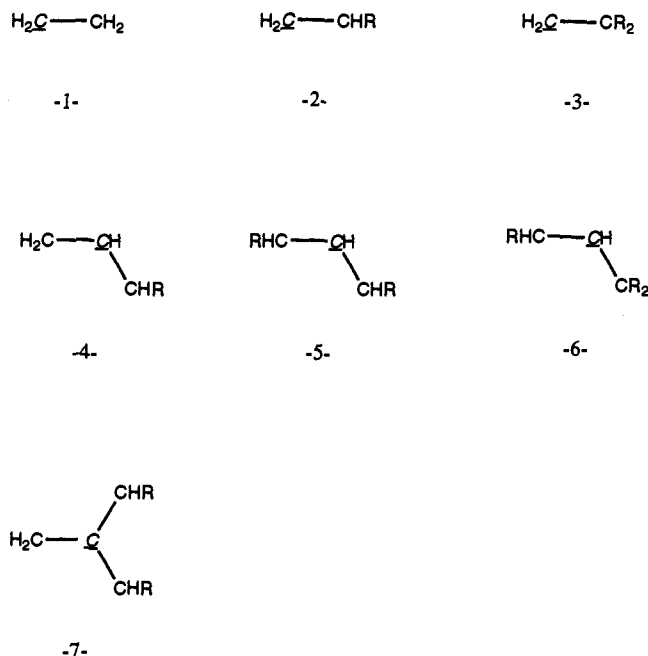
Figure 3. Types of carbon atoms.

Table 11. Comparison of Calculated Principal Values of Carbon Shielding Tensors and Those Given in Table 10 for Different Bonding Situations in Polyenes[a]

type[b]	molecule	atom	$\sigma_{33}(zz)$	σ_{22}	σ_{11}	σ_{av}
1–7[c]			176	83	−65	66
			22	31	25	20
5, CHR			165.2	81.8	−55.3	63.9
			12.8	5.5	7.8	6.0
	1a		191.7	49.8	−60.3	60.4
	1b		193.6	52.8	−56.1	63.4
	2a		186.5	56.5	−61.7	60.4
	2b		188.3	59.7	−56.1	64.0
	3	C_1	161.6	70.9	−68.8	54.6
	4	C_1	157.1	45.8	−96.5	35.5
	6	C_1	161.3	75.8	−69.1	56.0
7, CR_2			176.8	59.6	−80.2	52.1
			2.4	7.7	4.0	3.2
	3	C_5	155.9	48.6	−82.4	40.7
	4	C_3	145.4	55.4	−80.9	40.0
	5	C_1	212.4	45.9	−51.6	68.9
3, CH_2			172.6	101.3	−43.3	76.3
			18.2	11.2	8.6	12.3
	3	C_6	168.3	67.3	−48.6	62.3
	4	C_5	185.7	111.2	−7.5	96.4
	5	C_4	184.0	88.3	−5.4	89.0
6, CHR			163.1	79.6	−75.4	55.7
			18.8	3.0	2.4	7.2
	3	C_3	162.9	87.1	−62.2	62.6

[a] As in Table 10 for each type average values and maximum deviations (in absolute value) are given in consecutive lines. [b] See also Figure 3. [c] Averages of types 1–7.

polyenes and 27 ppm above the value of its type (**5**). It would be too premature to conclude that this somewhat enhanced shielding is a ring current effect.

For the two other (deshielded) components, σ_{22} and σ_{11}, the variations are larger and less systematic. Again the systems with small rings show the largest deviations. Comparing the C-atom in benzene with polyene C-atoms of the same type, the deviation is small for σ_{11}, but significant for σ_{22}. On the other hand the benzene C-atom differs rather little from the C-atoms of type 5 in the other ring systems as far as σ_{11} and σ_{22} are concerned.

6. Conclusions

While the evidence from experimental results on ring current effects has been rather indirect, in terms of IGLO calculations these effects can be detected directly. The evidence becomes

even stronger if one takes this study as complementary to that of idealized Hückel annulenes[40] and of the antiaromatic cyclobutadiene[41] and a direct study of the ring currents in physical space.[21] A recent study of Bader and Keith[42] is also consistent with our findings.

Ring currents affect the susceptibility (mainly its anisotropy) strongly, but have—in the case of benzene—only a small effect on the ^{1}H shift and probably no detectable effect on the ^{13}C shift. Some delocalization effects to be regarded as precursors of a ring current appear to play a role in fulvene and cyclopentadiene, but are really manifest only in the susceptibility anisotropy, not in the ^{1}H shifts.

A reader who knows that the IGLO method uses the concept of localized molecular orbitals (LMO) and that the quantities obtained in IGLO calculations are sums of MO contributions may want to ask two questions.

1. Is a method based on LMOs able to account for ring current effects, which have obviously something to do with electron delocalization?

2. Does the fact that IGLO calculations account for all observations not imply that all what one observes, e.g. for benzene, can be perfectly described in terms of local quantities and hence confirm Musher's refutation[15] of the ring current picture?

The answer to the first question is that the π-system in benzene can be described in terms of three LMOs mainly localized in one of the three double bonds of a Kekulé structure, but with "localization defects" that guarantee that benzene has an overall D_{6h} symmetry. These LMOs look, in fact, different from genuinely localized orbitals,[21] but they have all the properties for the IGLO method to work.

This already gives a partial answer to the second question. The χ and σ tensors are, in fact, obtained as sums of LMO contributions, but the contributions of the three LMOs that describe the π-system in benzene are very different from MO contributions of a genuine double bond. So Musher is somehow right that a description of the magnetic properties of benzene is possible in terms of localized quantities. However, these must not be taken over from molecules with genuinely localized bonds. Even in the LMO description on which IGLO is based, the delocalized nature of the π-system is implicitly taken care of.

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Appendix

Derivation of the IGLO Increment System. To get an increment system separately for the in-plane and out-of-plane components of the susceptibility from IGLO calculations of ethylene (χ_{zz} = -27.4 ppm cgs, χ_{ip} = -20.0 ppm cgs) and the average of *cis*- and *trans*-butadiene (χ_{zz} = -50.0 ppm cgs, χ_{ip} = -35.0 ppm cgs), we first note that these molecules consist of the following bonds:

$$\text{ethylene: } 1 \text{ C=C, } 4 \text{ CH}$$

$$\text{butadiene: } 2 \text{ C=C, } 1 \text{ C-C, } 6 \text{ CH}$$

From the data of ethylene and butadiene of Table 2 we get for the difference between one C–C and two CH increments:

$$1 \text{ C-C minus } 2 \text{ CH: ip 5.0 ppm cgs}$$

$$1 \text{ C-C minus } 2 \text{ CH: } zz \text{ 4.9 ppm cgs}$$

Noting that

$$\text{hexatriene: } 3 \text{ C=C, } 2 \text{ C-C, } 8 \text{ CH}$$

we predict from the increment system and the data for ethylene

$$\text{hexatriene(inc): } \chi_{ip} = -50.1; \chi_{zz} = -72.5$$

With respect to this prediction χ_{ip} for the various hexatrienes in Table 2 scatters by only a few tenths of a ppm cgs and χ_{zz} by ±3 ppm cgs, which indicates that the noncyclic polyenes are rather well described by the increment system.

For a hypothetical polyene-like cyclohexatriene (or any isomers with three double bonds) we have

$$\text{cyclohexatriene: } 3 \text{ C=C, } 3 \text{ C-C, } 6 \text{ CH}$$

which corresponds to 3 times ethylene + 3 times (C–C minus 2 CH), i.e.

$$\text{cyclohexatriene(inc): } \chi_{ip} = -45.1 \text{ ppm cgs;}$$

$$\chi_{zz} = -67.7 \text{ ppm cgs}$$

In order to get an increment system that allows us a prediction for non(hyper)conjugated cyclopentadiene, we note that

$$1,4\text{-cyclohexadiene: } 2 \text{ C=C, } 4 \text{ C-C, } 4 \text{ CH, } 2 \text{ CH}_2$$

$$\text{cyclopentadiene: } 2 \text{ C=C, } 3 \text{ C-C, } 4 \text{ CH, } 1 \text{ CH}_2$$

We can predict the increment value for cyclopentadiene as

$$^1/_2\text{cyclohexadiene plus butadiene minus ethylene}$$

assuming that there is no hyperconjugation in cyclohexadiene. The result is

cyclopentadiene(inc): χ_{ip} = -26.5 -35.0 + 20.0 =

-41.5 ppm cgs; χ_{zz} = -31.4 -50.0 + 27.4 = -53.9 ppm cgs

while the values actually calculated for cyclopentadiene are

$$\chi_{ip} = -40.8 \text{ ppm cgs; } \chi_{zz} = -70.9 \text{ ppm cgs}$$

The actual $|\chi_{zz}|$ is hence ~17 ppm cgs larger than the value predicted by the increment system.