boranes. Equation 5 shows the relationship between the charge-transfer transition frequency of a D-TCNE complex (where D is a benzene derivative) and the ionization energy of the donor (I_D). Substituting the frequencies at maximum absorbance for the triarylborane-TCNE complexes (Table V) into eq 5, we obtain the values 9.2, 8.9, and 8.5 eV for TPB, TOTB, and TMB. The corresponding experimental values for benzene, toluene, and mesitylene are 9.24, 8.82, and 8.93 eV.[24]

The triarylborane-TCNE complexes are similar to corresponding benzene-TCNE complexes in all but two respects. First of all, the molar absorptivities of the former are an order of magnitude smaller. Secondly, the K value for TMB-TCNE (2.4) is much smaller than that of mesitylene-TCNE (17.3). This anomaly may be due to interference from the six ortho methyl groups which partially cover the six faces of phenyl rings of TMB. Examination of space-filling models of TMB (Figure 2) and TCNE show that effective overlap of the bπ and aπ orbitals is blocked by these methyl groups. Steric effects have been used to account for the large difference in K values between the TCNE complexes of hexamethylbenzene (16.9) and hexaethylbenzene (0.32);[7] they may also account for the differences between TMB-TCNE and mesitylene-TCNE.

The existence of many electron donor-acceptor complexes between aromatic hydrocarbons and iodine, bromine, and iodine monochloride has been established and their characteristics have been exhaustively studied, documented and reviewed.[25] It is therefore remarkable that no spectral evidence for triarylborane-halogen complexes has been observed. Either the triarylborane-halogen complexes do not form, of if they do, the charge-transfer bands of these complexes are covered by the absorbance bands of the triarylboranes themselves.

Acknowledgment. We are grateful for financial support from a Northern Michigan University Faculty Research Grant and to Lynn Podehl for valuable technical assistance.

Registry No. TPB·TCNE, 84961-35-3; TOTB·TCNE, 84961-36-4; TMB·TCNE, 84961-37-5; TPB, 960-71-4; TMB, 7297-95-2; ICl, 7790-99-0.

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Conformational, Bond-Order, and Substituent Dependencies of Orthobenzylic Coupling Constants

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Abstract: Because they are a potential source of valuable structural information, experimental and theoretical results are reported for the bond-order, conformational, and substituent dependencies of the long range H-H coupling constants over four bonds (orthobenzylic coupling, J_{ob}) between protons on an sp^3-hybridized α-carbon atom and the ortho protons of aromatic systems. A large number of methyl aromatic systems were synthesized and their coupling constants were accurately measured. The best correlations in this series of compounds were with the square of the mobile π-bond order and with the mutual atom-atom polarizability $\pi_{pp'}$. In addition, several series of compounds with defined geometries and a range of dihedral angles were synthesized and the ^{1}H NMR parameters were measured. The best agreement of the data is with a semiempirical equation, which relates the orthobenzylic coupling constant to $\pi_{pp'}$ and to dihedral angles according to the equation $J_{ob}(\phi,\pi_{pp'}) = 6.90\ \pi_{pp'} \sin^2 \phi - 0.32 \cos^2 \phi$ Hz. Substituent effects on J_{ob} are not usually important; exceptions are found in the 1-substituted acenaphthene derivatives, in which J_{ob} becomes more positive with increasing electronegativity, and in ring-substituted toluenes, having both a nitro and an oxygen group which exert significant bond-fixing effects.

Introduction

The nuclear spin-spin coupling between a proton attached to an sp^3-hybridized α-carbon atom of a side chain and the aromatic protons of a benzene ring is a special case of the more general phenomenon of benzylic coupling.[2-5] In fact, it has been noted[4] that benzylic coupling is a rather arbitrary subdivision of the larger class of coupling constants between protons attached to any benzylic atom and ring protons and includes coupling through heteroatoms.[6-8]

Of the various types of benzylic couplings the most widely investigated[2-13] has been orthobenzylic (J_{ob}) which refers to coupling between protons on the α-carbon atom and an ortho proton of the toluene moiety **1**. Coupling between the benzylic protons and meta and para hydrogens are called meta- and parabenzylic, respectively. The decreased magnitudes of experimental orthobenzylic coupling constants (for toluene $J_{ob} = -0.75$

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(1) (a) University of Arizona. (b) University of Sydney.

(2) This term seems to have been introduced by Nair, P. M.; Gopakumar, G. *Tetrahedron Lett.* **1964**, 709.

(3) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance in Organic Chemistry"; Pergamon Press: New York, 1968, Chapter 4-4.

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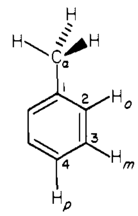
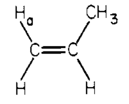
0002-7863/83/1505-2178$01.50/0



1



2

Hz, for example[14]) relative to the cisoid allylic coupling constant [$^4J_{csd} = {}^4J(CH_3, H_a) = -1.75$ Hz[15]] in propene **2**, is attributable to the decrease in the mobile π-bond order below unity in the aromatic moiety.

In the first part of this study a number of methyl aromatic compounds were synthesized and the NMR coupling constants were accurately measured with the goal of more precisely investigating the dependence of J_{ob} over the whole range of bond orders and mutual atom–atom polarizabilities. Experimental data for the metabenzylic J_{mb} and parabenzylic J_{pb} coupling constants are so scanty and unreliable that a satisfactory correlation with bond order cannot yet be made. Previous studies from these laboratories[16,17] have been concerned with $^4J_{HH'}$ in propanic and allylic fragments. These represent the extremes of π-bond orders for this type of coupling.

Benzylic coupling constants depend on the dihedral angle ϕ measured about the C_1–C_α bond in **1**. This angle is measured from the plane of the aromatic ring as depicted in Figure 1. A large number of compounds with benzylic protons in fixed orientations were synthesized and the coupling constants were measured to establish the conformational dependence of J_{ob}. A single mathematical expression which combines both the "bond order" and conformational dependence of J_{ob} is obtained and is found to be in excellent agreement with the experimental data. It was also of interest to investigate the importance of substituents including the role of bond fixation and solvents on J_{ob}.

The Relationship of Coupling Constants to Bond Orders and Mutual Atom–Atom Polarizabilities

The connection[18] between coupling constants and bond orders has been extensively used in the interpretation of nuclear spin–spin coupling constants. McConnell[18] used a molecular orbital (MO) description, and the "average energy approximation" applied to the Fermi contact mechanism, to relate the π-electron contribution $J^{\pi}{}_{HH'}$ to the mobile π-bond order[19,20]

$$J^{\pi}{}_{HH'} = (4h\Delta E)^{-1} a_H a_{H'} \eta^2{}_{pp'} \qquad (1)$$

where h is Planck's constant, ΔE is an average excitation energy, a_H and $a_{H'}$ are ESR hyperfine coupling constants for related free radical fragments, and $\eta_{pp'}$ is the MO π-bond order[21] associated with 2p atomic orbitals p and p′ in the unsaturated or aromatic moiety. Hyperfine coupling constants a_H for the C–CH$_3$ moiety have a theoretical dependence on dihedral angle about the C–C bond of the form[22]

$$a_H = A \sin^2 \phi + B \qquad (2)$$

where $A \simeq 150$ MHz and $B \simeq 0$,[23] and the dihedral angle ϕ is measured from the plane perpendicular to the 2p atomic orbital. Since the hyperfine coupling constant $a_{H'}$ for a C–H radical is a constant, the angular dependence of the π-electron contribution to the benzylic coupling constants is of the form of eq 2.

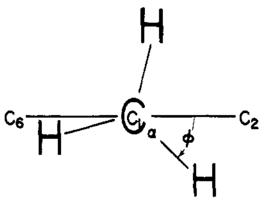


Figure 1. Specification of the dihedral angle ϕ in toluene and other benzylic compounds. The dihedral angle is measured between the plane of the aromatic ring and the plane formed by H–C_α–C_1.

Table I. Comparison of Calculated and Experimental Results for Benzylic Coupling Constants in Toluene[a]

method	J_{ob}	J_{mb}	J_{pb}
MO, eq 1[b,c]	−0.42	0	−0.11
MO, eq 3[b,d]	−0.30	0.02	−0.20
SCF-MO[e]	−0.31	0.06	−0.38
SCF-MO-CI[e]	−0.67	0.33	−0.62
INDO-FPT[f]	−0.92	0.69	−0.64
experiment[g]	−0.75	0.36	−0.62

[a] All values in hertz. [b] $a_H = 75$ MHz, $a_{H'} = -63$ MHz, $\Delta E = -2\beta = 5.12$ eV. [c] $\eta_{12} = 0.667$, $\eta_{13} = 0$, $\eta_{14} = 0.33$. [d] $\pi_{12} = -0.157$, $\pi_{13} = 0.009$, $\pi_{14} = -0.102$, $\beta = -2.56$ eV. [e] Reference 32. [f] Reference 34. [g] Reference 14.

The assumption of the "average energy approximation" and single determinant MO theory causes some serious difficulties with eq 1;[5] $\eta_{pp'}$ vanishes identically if p and p′ are in the same subset of an alternant system so that J_{mb} are identically zero. Calculated values of J_{ob}, J_{mb}, and J_{pb} for toluene are given in Table I along with the experimental data.

In valence-bond descriptions, which invoke the "average energy approximation",[24,26] the π-electron contributions are linearly related to the Penney-Dirac bond orders.[27] Since these are negative for p-orbitals on C1 and C3 of toluene, the correct sign of J_{mb} is predicted.[25,28]

Many of the difficulties encountered on using the "average energy approximation" are avoided in formulations which include explicit sums over excited state wave functions[29] in the second-order perturbation formulation.[30] A number of expressions for the π-electron contributions have been suggested.[29] Of particular interest for the purposes of this investigation is the relationship[31] of the π-electron contribution to the mutual atom–atom polarizability $\pi_{pp'}$

$$J^{\pi}{}_{HH'} = (1/4) a_H a_{H'} \pi_{pp'} \beta^{-1} \qquad (3)$$

where β is the usual resonance integral of Hückel molecular orbital (HMO) theory. Benzylic coupling constants based on eq 3 and the parameters adopted by Acrivos[28] are also included in Table I. In all cases the magnitudes are smaller than the experimental ones. The reasons for the inadequacy of this approximation can be seen in terms of perturbation theory with SCF wave functions[32] corresponding to uncoupled Hartree–Fock method b.[33] These results in Table I are comparable to those obtained from eq 3. However, the inclusion of configuration interaction (CI) in the triplet manifold gives results[32] in substantially better agreement with the experimental data in Table I.

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(20) This expression was given incorrectly in ref 17.

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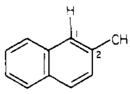
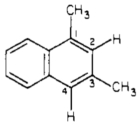
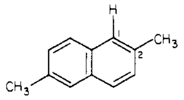
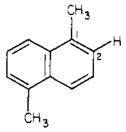
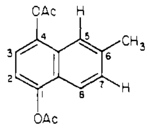
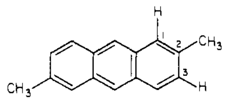
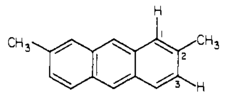
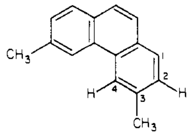
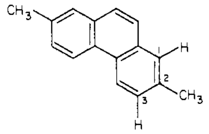
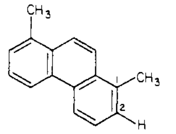
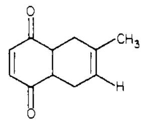
Table II. Orthobenzylic Coupling Constants, Bond Orders, and Mutual Atom-Atom Polarizabilities for Methylaromatic Compounds and Compound 13, Which Has a Vinylic Methyl Group

compd no.	structure	J_{ob}, Hz[a]	$\eta_{pp'}$	$-\pi_{pp'}$
3		$J(\text{Me-H}_1) = -1.05$	0.725	0.213
4		$J(\text{1-Me-H}_2) = -1.11$ $J(\text{3-Me-H}_2) = -0.45$ $J(\text{3-Me-H}_4) = -1.06$	0.725 0.603 0.725	0.213 0.110 0.213
5		$J(\text{Me-H}_1) = -0.84$	0.725	0.213
6		$J(\text{Me-H}_2) = -0.90$	0.725	0.213
7		$J(\text{Me-H}_5) = -1.00$ $J(\text{Me-H}_7) = -0.47$	0.725 0.603	0.213 0.110
8		$J(\text{Me-H}_1) = -1.04$ $J(\text{Me-H}_3) = -0.3 \pm 0.1$	0.737 0.586	0.230 0.099
9		$J(\text{Me-H}_1) = -0.9 \pm 0.1$ $J(\text{Me-H}_3) = -0.3 \pm 0.1$	0.737 0.586	0.230 0.099
10		$J(\text{Me-H}_2) = -0.45$ $J(\text{Me-H}_4) = -0.82$	0.623 0.702	0.124 0.189
11		$J(\text{Me-H}_1) = -0.83$ $J(\text{Me-H}_3) = -0.51$	0.707 0.623	0.194 0.124
12		$J(\text{Me-H}_2) = -0.91$	0.707	0.194
13		$J(\text{Me-H}_7) = -1.7 \pm 0.1$	1.000	0.500

[a] Coupling constants are assumed to be accurate to ±0.05 Hz unless otherwise specified.

Also included in Table I are the calculated results[34] based on finite perturbation theory (FPT) in the semiempirical SCF-MO approximation of intermediate neglect of differential overlap (INDO).[35] As this is an all-valence electron scheme, certain types of σ-electron contributions are included in contrast to the other calculated results in Table I.

Although the more sophisticated MO calculations give results in better conformity with the experimental benzylic coupling constants in Table I, these calculations become increasingly difficult in the larger aromatic system of interest in this study. As a consequence, it will be of interest to investigate the applicability of empirical correlations of experimental coupling constants with bond orders and mutual atom-atom polarizabilities.

Bond Order and Substituent Dependence of J_{ob} in Methyl-Substituted Aromatic Compounds

To investigate the applicability of correlations of orthobenzylic coupling constants with bond orders and mutual atom-atom polarizabilities, a number of methyl-substituted aromatic compounds were synthesized and their spectral parameters were determined.[36]

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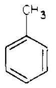
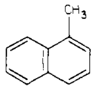
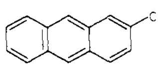
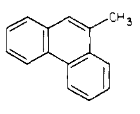
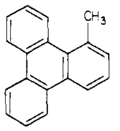
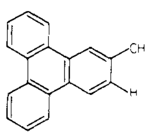
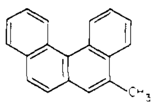
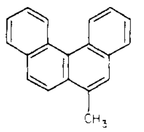
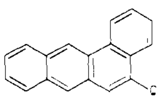
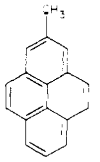
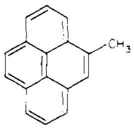
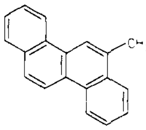
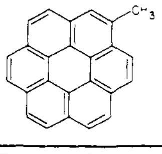
[35] Pople, J. A.; McIver, J. W., Jr.; Ostlund, N. S. *J. Chem. Phys.* **1968**, *49*, 2960, 2965.

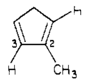
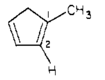
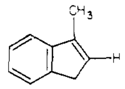
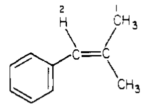
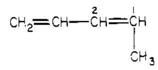
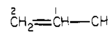
[36] Supplementary material.

Table III. Orthobenzylic Coupling Constants, Bond Orders, and Mutual Atom-Atom Polarizabilities for Methyl-Substituted Aromatic Compounds

compd no.	structure	J_{ob}, Hz	$\eta_{pp'}$	$-\pi_{pp'}$	ref
1		−0.75	0.667	0.157	14
14		−0.7	0.725	0.213	12
15		−0.8	0.737	0.230	12
16		−1.10	0.760	0.269	9, 10, *a*
17		−0.5	0.690	0.177	10
18		−0.5	0.637	0.134	10
19		−0.8	0.765	0.252	*b*
20		−1.0	0.765	0.252	*b*
21		−1.2	0.783	0.284	*b*
22		−0.72	0.669	0.159	*d*
23		−1.16	0.777	0.274	*d*
24		−1.0	0.754	0.245	*c*
25		−0.9	0.745	0.232	*a*

[a] Clar, E.; McAndrew, B. A.; Zander, M. *Tetrahedron* 1962, *23*, 985; Clar, E.; Sanigök, Ü.; Zander, M. *Ibid.* 1968, *24*, 2817; Clar, E.; Mullen, A.; Sanigök, Ü.; *Ibid.* 1969, *25*, 5639; Clar, E.; McAndrew, B. A.; Sanigök, Ü.; *Ibid.* 1970, *26*, 2099; Clar, E.; Mackay, C. C. *Ibid.* 1971, *27*, 5943; Clar, E.; Mackay, C. C. *Tetrahedron Lett.* 1970, 871. [b] Ouellette, R. J.; van Leuwen, B. J. *J. Org. Chem.* 1969, *34*, 62. [c] Cagniant, D. *Bull. Soc. Chim. Fr.* 1966, 2325. [d] M. J. Collins, unpublished data, 1982.

Table IV. Cisoid Allylic Coupling Constants J_{csd}, MO Bond Orders $\eta_{pp'}$, and Mutual Atom-Atom Polarizabilities $\pi_{pp'}$ for Compounds Having a Vinylic Methyl Group

compd no.	structure	J_{csd}	$\eta_{pp'}$	$-\pi_{pp'}$	ref
26		J(Me-H$_1$) = −1.5	0.894	0.402	*a*
		J(Me-H$_3$) = −0.4	0.447	0.045	
27		J(Me-H$_2$) = −1.6	0.894	0.402	*a*
28		J(Me-H$_2$) = −1.66	0.911	0.419	*b*
29		J(1-Me-H$_2$) = −1.53	0.911	0.419	*c*
30	 $CH_2{=}CH{-}\overset{2}{C}H{=}\underset{CH_3}{\overset{1}{C}H}$	J(Me-H$_2$) = −1.61	0.894	0.402	*d*
2	 $\overset{2}{C}H_2{=}\overset{1}{C}H{-}CH_3$	−1.75	1.000	0.500	*e*

[a] Korenevsky, V. A.; Sergeyev, N. M. *J. Am. Chem. Soc.* 1972, *94*, 8586. [b] Bergson G.; Weidler, A.-M. *Acta Chem. Scand.* 1963, *17*, 862. [c] Curry, E. R.; Sardella, D. J. *J. Am. Chem. Soc.* 1974, *96*, 1822. [d] Segre, A. L.; Zetta, L.; Di Corato, A. *J. Mol. Spectrosc.* 1969, *32*, 296. [e] Reference 15.

The J_{ob} are given in Table II along with available HMO bond orders $\eta_{pp'}$ and mutual atom-atom polarizabilities $\pi_{pp'}$[37] for the parent polyacenes. The parameters for the latter were based on the usual HMO approximation of equal resonance integrals and, therefore, do not include the effects of different bond lengths or substituent effects such as those due to the methyl groups. In Table III are listed some additional tabulated orthobenzylic coupling constant data from the literature. Most of the values are less accurate than those in Table II.

In Tables II and III several of the entries have methyl substituents next to ring junctions; these might have been considered unsuitable because of possible steric effects. However, the values for these compounds are not substantially different from related isomers so that it will be assumed that steric effects in these compounds are negligible.

Data in Table II indicate that J_{ob} varies more than the range of error; e.g., in the dimethylnaphthalenes **4** and **5** J_{ob} ranges from −0.84 to −1.11 Hz. This difference is outside the range of experimental error and suggests that factors other than bond order/polarizability are significant in polycyclic systems. Factors which could contribute to these disparities are subtle but could relate to the substituent effects of C1 vs. C2 substitution on the bond lengths and bond orders.

In addition to the cisoid allylic coupling constant J_{csd} in propene, several values of J_{csd} are given in Table IV for cyclic and alicyclic polyenes for which the bond orders are reduced below unity.

The linear and quadratic dependence of J_{ob} on bond orders has been discussed extensively in previous studies.[2-13] Linear least-squares analysis of the much larger sets of data in Tables II–IV gives

$$J_{ob}(\eta_{pp'}) = -3.45\eta_{pp'} + 1.58 \qquad (4)$$

with correlation coefficient $r = 0.96$. Those data in the relevant tables, which were considered to be of sufficient accuracy to be cited to better than 0.1 Hz, were weighted four times the others. The major effect of this weighting was to reduce the standard deviations in the slope and intercept. The intercept corresponds to π bond order zero and should not be substantially different from

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(37) Coulson, C. A.; Streitweiser, A., Jr. "Dictionary of π-Electron Calculations"; W. H. Freeman Co.: San Francisco, CA, 1965.

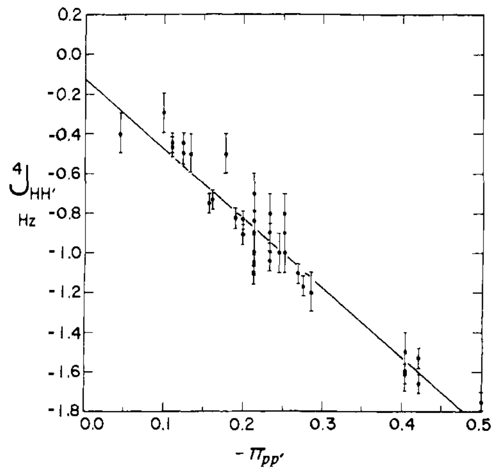


Figure 2. A plot of the experimental J_{ob} (and J_{csd}) coupling constant data from Tables II and III as a function of the mutual atom–atom polarizability $\pi_{pp'}$. The straight line in the figure was obtained from a linear least squares analysis of the data (eq 10).

coupling over four bonds involving a methyl group in the cis orientation of a saturated moiety. Previous studies[16] of this type of coupling indicate that it is in the range of +0.15 Hz to −0.17 Hz, or a small fraction of that implied in eq 4. Since there is no theoretical basis for a linear correlation of J_{ob} with MO bond order $\eta_{pp'}$, it is not surprising that eq 4 appears to be inconsistent with the experimental data in the region of small bond orders.

A linear least-squares analysis of the data also yields

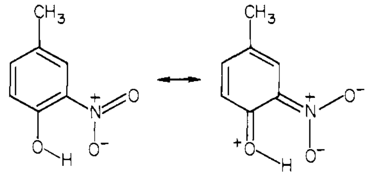
$$J_{ob}(\eta_{pp'}) = -2.20\eta^2_{pp'} + 0.25 \qquad (5)$$

with correlation coefficient $r = 0.95$. The smaller intercept is in better conformity with the experimental data in saturated systems.[16] However, an objection which has been raised to the use of eq 1 is that the average excitation energy ΔE should not be the same for aromatic and unsaturated hydrocarbons;[12] hence different slopes and intercepts might be expected for the two classes of compounds. Since the formulation leading to eq 3 does not make the "average energy approximation", this objection should not be applicable. Accordingly, the J_{ob}/J_{csd} data from Tables II–IV are plotted in Figure 2 as a function of the mutual atom–atom polarizabilities. The various data were assumed to be accurate to either ±0.05 or ±0.1 Hz in preparing this plot. However, the latter figure may be much too optimistic for some of the earlier experimental data. A linear least-squares treatment of experimental data leads to the straight line in the figure

$$J_{ob}(\pi_{pp'}) = 3.45\pi_{pp'} - 0.16 \qquad (6)$$

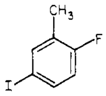
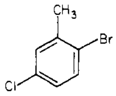
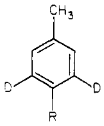
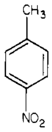
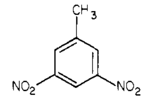
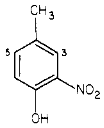
with correlation coefficient $r = 0.96$. The intercept of −0.16 Hz falls within the range observed in saturated moieties[16] in which the methyl group and the hydrogen have the cisoid arrangement. Equations 5 and 6 will be used in the subsequent analysis of the conformational dependence of J_{ob}.

Benzylic coupling constants J_{ob} in ring substituted toluenes show relatively small substituent effects as can be seen from representative data in Table V. Exceptions are those cases in which the substituents cause appreciable bond fixation. For example, consider the case of 2-nitro-4-methylphenol **36** in Table V for which there are substantial deviations from the toluene value of J_{ob}. The rather substantial deviations from the toluene value are attributable to the effects of bond fixation associated with the importance of the canonical forms



to the ground state wave function.

Table V. Orthobenzylic Coupling Constants for Ring-Substituted Toluenes

compd no.	structure	R	J_{ob}	ref
31			−0.73	*a*
32			−0.63	*b*
33		CN COOMe NH_2 $NMe_3^+I^-$ Cl OH	0.71 0.69 0.68 0.70 0.71 0.69	*b*
34			−0.75	*c*
35			−0.75	*c*
36		$J(CH_3,H3) = -1.00$ $J(CH_3,H5) = -0.62$		*d*

[a] Albriktsen, P.; Hansen, G. *Acta Chem. Scand.* 1972, *26*, 2511. [b] Kotowycz, G.; Schaefer, T. *Can. J. Chem.* 1966, *44*, 2743. [c] Gehring, D. G.; Reddy, G. S. *Anal. Chem.* 1968, *40*, 792. [d] This work.[36]

In a study of bond fixation in 2-pyrones, Sardella et al.[38] estimated the π-bond orders from the experimental coupling constants and the equation of Bartle et al.[10] A comparison of the experimentally estimated bond orders with those based on MO calculations indicated better agreement for high bond orders than for low. Equation 5 gives better agreement over the whole range of π-bond orders.

The Conformational Dependence of Orthobenzylic Coupling Constants

The angular dependence of the π-electron contributions to the orthobenzylic coupling constants is obtained on substituting eq 2 into either eq 1 or eq 3. Assuming that B in eq 2 is negligible in comparison with A, then both bond order and angular features are contained in the simple equations

$$J_{ob}^{\pi}(\phi,\eta_{pp'}) = 2A'\eta^2_{pp'} \sin^2 \phi \qquad (7)$$

$$J_{ob}^{\pi}(\phi,\pi_{pp'}) = 2A''\pi_{pp'} \sin^2 \phi \qquad (8)$$

where A' and A'' are constants which can be inferred from eq 1 and 3, but which will be determined empirically from the results of the previous section, and ϕ is the dihedral angle measured from the plane of the rings in aromatic compounds and from the $2p_\pi$ plane in unsaturated molecules. Assuming either free rotation or hindered rotation of the methyl group,[39,40] the average values for eq 7 and 8 are $A'\eta^2_{pp'}$ and $A''\pi_{pp'}$, respectively. The coefficients A' and A'' may, therefore, be taken to be the slopes in eq 5 and 6, and the intercepts are assumed to be the rotationally averaged σ-electron contributions, J^{σ}_{ob}.

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(38) Sardella, D. J.; Holak, T.; Vogel, G. *Org. Magn. Reson.* **1975**, *7*, 355.
(39) Lide, D. R., Jr. *J. Chem. Phys.* **1958**, *29*, 1426; Wilson, E. B., Jr. *Advan. Chem. Phys.* **1959**, *2*, 367.
(40) Herschbach, D. R.; Krisher, L. C. *J. Chem. Phys.* **1958**, *28*, 728.
(41) Fallick, C. J., Ph.D. Thesis, University of Sydney, 1975.
(42) Hata, K. Ph.D. Thesis, University of Sydney, 1980.

Table VI. Calculated Values of the Orthobenzylic Coupling Constants in Toluene Based on the INDO-FPT Method and by Means of Eq 9 and 10 for 30° Intervals of the Dihedral Angle ϕ

dihedral angle ϕ, deg	INDO-FPT[a]	J_{ob}, Hz, eq 9[b]	eq 10[c]
0	−0.34	0.50	−0.32
30	−0.61	−0.11	−0.51
60	−1.15	−1.34	−0.89
90	−1.47	−1.96	−1.08
120	−1.26	−1.34	−0.89
150	−0.81	−0.11	−0.51
180	−0.58	0.50	−0.32

[a] Taken from Table I of ref 34. [b] With $\eta_{pp'} = 0.667$. [c] With $\pi_{pp'} = -0.157$.

The factors affecting σ-electron coupling over four bonds are complex. Experimental and theoretical studies[16,17] of cisoid allylic coupling indicate symmetry about $\phi = 90°$, thereby suggesting a simple $\cos^2 \phi$ dependence on dihedral angle. With this further assumption, eq 5–8 can be combined into forms which combine both the "bond order" and angular features of orthobenzylic coupling/cisoid allylic coupling.

$$J_{\text{ob}}(\phi,\eta_{pp'}) = -4.40\eta^2_{pp'} \sin^2 \phi + 0.50 \cos^2 \phi \tag{9}$$

$$J_{\text{ob}}(\phi,\pi_{pp'}) = 6.90\pi_{pp'} \sin^2 \phi - 0.32 \cos^2 \phi \tag{10}$$

In the case of propene with the assumption of either free rotation or an average over three equivalent rotamer populations,[43] eq 9 and 10 give $J_{\text{csd}} = -1.95$ Hz and −1.88 Hz, respectively, in comparison with the experimental value of −1.75 Hz.[15] Orthobenzylic coupling constants for toluene ($\eta_{pp'} = 0.667$, $\pi_{pp'} = 0.157$) from eq 9 and 10 are given in Table VI at 30° intervals of the dihedral angle ϕ. Also included in the table are previously reported[34] INDO–FPT results. Equation 10 is in better correspondence with the INDO–FPT results except for dihedral angles in the range 120–150°. The average values for toluene based on the INDO–FPT method,[34] eq 9, and eq 10 are −0.92, −0.73, and −0.70 Hz, respectively, in comparison with the experimental value of −0.75 Hz.[14] The more negative values in the all-valence electron INDO scheme are probably due to an overestimation of the magnitudes over the whole range of dihedral angles, an inadequacy noted in our previous work on cisoid allylic coupling constants.[16,17]

To investigate the experimental dependence of J_{ob} on conformational effects, a large number of compounds were synthesized and their NMR parameters were measured.[36] Molecules were chosen so that the dihedral angles of the benzylic protons varied over the whole range of 0–180°. Experimental values of J_{ob} and estimated dihedral angles are given in Table VII. These are, in fact, representative values from an extensive compilation,[41,42] and an even larger group which was excluded because of uncertainty of conformation, known bond fixation, or substituent effects. However, for practical reasons, it was not possible to exclude entirely the latter, but it appears from a great many measurements (of which those in Table VII are typical) that the J_{ob} are not greatly sensitive to substituent effects.

In only a few cases have signs of orthobenzylic coupling constants been determined in rigid structures. However, the averaged values in toluene and its derivatives are well-established as negative, and all calculated values are negative independent of dihedral angle. The sign determinations for structure **39** indicate that $J_{\text{ob}}(\sim 10°)$ and $J_{\text{ob}}(\sim 170°)$ are both negative. Therefore, with the exception of the results for **39**, all coupling constants in Table VII are assumed to be negative by analogy.

The experimental values from Table VII are plotted in Figure 3 as a function of the dihedral angle ϕ. The circles representing the data points are crudely indicative of the errors in the measured values of J_{ob} and the estimated dihedral angles. Because dihedral angles were inferred from Dreiding stereo models, errors in dihedral angles could be larger. The values of $\pi_{pp'}$ for entries **40**, **42**, and **45** in Table VII would be somewhat larger than the value in benzene because of the extension of conjugation involving the carbonyl and aromatic functions. Since the increases in the magnitudes of $\pi_{pp'}$ are less than 5%, a correction of the data would change the values by an amount less than the experimental error. Only limited coupling constant data are available for compounds with dihedral angles greater than 90° because such geometries are uncommon.

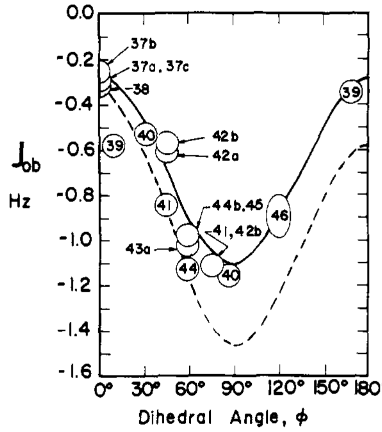
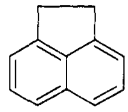


Figure 3. Experimental values of J_{ob} from Table VII for substances of defined geometry plotted as a function of the dihedral angle ϕ. The circles are taken to be crudely indicative of the errors in the measurements of coupling constants and estimates of dihedral angles. The dashed curve is the theoretical one based on the INDO–FPT results from ref 34 and partly reproduced in Table VI. The solid curve was based on eq 10 which is tabulated for $\pi_{pp'} = -0.157$ in Table VI.

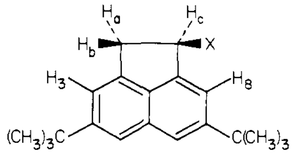
Also plotted in Figure 3 as a function of the dihedral angle ϕ are the calculated J_{ob} data for toluene from Table VI. The dashed line corresponds to the INDO–FPT MO results,[34] which fall below the experimental points for dihedral angles greater than about 60°. This is quite similar to the behavior noted for the INDO method applied to cisoid allylic coupling constants.[16,17] Much better agreement was found in a method which combined mutually exclusive MO and VB contributions.[16]

The $J_{\text{ob}}(\phi, \eta = {}^2/_3)$ data from eq 9 and Table VI were not plotted in Figure 3 because they deviate substantially from the experimental points over most of the range of dihedral angles. As a consequence, eq 9 may not prove to be useful for "bond order"/conformational studies.

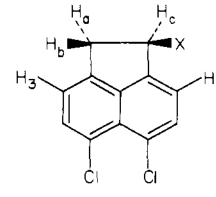
The orthobenzylic coupling constant data for eq 10 specialized to toluene with $\pi_{pp'} = -0.157$, and tabulated in the third column of Table VI, are plotted (solid line) as a function of ϕ in Figure 3. The agreement with the experimental data is excellent in view of the uncertainties in dihedral angles. This strongly suggests that eq 10 will be useful in the interpretation of the experimental data in systems in which both conformational and "bond order" effects determine the magnitude of the coupling constants. As an example, consider J_{ob} in acenaphthene **48**. Assuming dihedral angles


48

of 60° and $\pi_{pp'} = -0.213$, eq 10 gives a calculated orthobenzylic coupling constant of −1.19 Hz. Several compounds with the structures **49** and **50** were synthesized and their NMR parameters



49



50

were determined in the course of this study.[36] These are given

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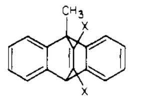
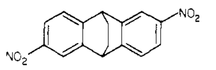
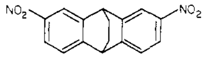
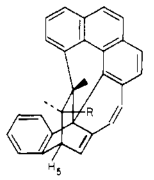
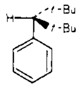
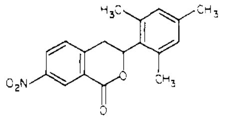
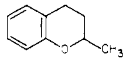
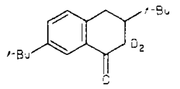
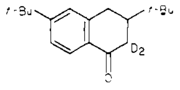
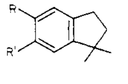
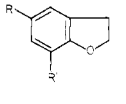
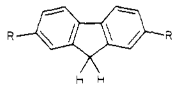
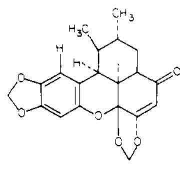
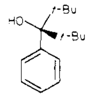
(43) Barfield, M. *J. Am. Chem. Soc.* **1971**, *93*, 1066.

Table VII. Orthobenzylic Coupling Constants in Molecules of Defined Configruation

compd no.	structure	J_{ob} [a] Hz	ϕ, deg
37a	 $X = CO_2CH_3$	$J_{4-10} = -0.29$	0
37b		$J_{4-10} = -0.26$	0
37c		$J_{4-10} = -0.28$	0
38	 $R = CO_2C_2H_5$	−0.31[c]	0
39		−0.58 −0.33	~10[b] ~170[b]
40		−0.53 −1.16	32 88
41		−0.84 −1.11	45 75
42a		−0.61 −1.13	45 75
42b		−0.58 −1.10	45 75
43		R R'	
		a CH_3 I −1.02[d]	60
		b CH_3O Br −1.00[d]	60
		c F NO_2 −1.02[d]	60
		d Cl NO_2 −1.09[d]	60
44		R R'	
		a H H −1.13	60
		b Cl H −1.17	60
		c CN H −1.22	60
		d NO_2 H −1.27	60
		e H NO_2 −1.32	60
		f Cl Cl −1.13	60
		g NO_2 NO_2 −1.45	60
45		R	
		a ND_2 −1.03	60
		b H −0.98	60
		c Cl −0.97	60
		d t-Bu −0.93	60
46		−0.8 to −1.0[e]	~120
47			b

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[a] Unless specified otherwise it is assumed that the coupling constants are accurate to ±0.05 Hz. [b] By analogy with 47, which has been studied by infrared and X-ray diffraction techniques [Hon, F. H.; Matsumura, H.; Tanida, H.; Tidwell, T. T. *J. Org. Chem.* **1972**, *37*, 1778; van Koningveld, H.; van Meurs, F. *Tetrahedron* 1977, *33*, 2699], 39 is probably not precisely planar, so that it is assumed that ϕ is about 10° and 170°. [c] The orthobenzylic coupling involves the H_5 proton at the bridgehead. The NMR spectrum was also analyzed by Martin, R. H.; Jespers, J.; Defay, W. *Helv. Chim. Acta* **1975**, *58*, 776. The sample used for the present study was a generous gift from Professor R. H. Martin. [d] Bott, G.; Field, L. D.; Sternhell, S. *J. Am. Chem. Soc.* 1980, *102*, 5618; Bott, G., unpublished results, 1980. [e] Brophy, G. C. M.Sc. Thesis, University of Sydney, 1972.

Table VIII. Substituent Dependence of Orthobenzylic Coupling Constants in 49 and 50

		49^b			50^b		
X	$E_x{}^a$	$J_{ob}(H_a\text{-}H_3)$	$J_{ob}(H_b\text{-}H_3)$	$J_{ob}(H_c\text{-}H_8)$	$J_{ob}(H_a\text{-}H_3)$	$J_{ob}(H_b\text{-}H_3)$	$J_{ob}(H_c\text{-}H_8)$
H	1.78	−1.49	−1.49	−1.49	−1.55	−1.55	−1.55
CH_3	2.07	−1.20	$-^c$	$-^c$	−1.26	$-^c$	$-^c$
$CH(CO_2CH_3)_2$	2.40	−1.26	−1.26	−1.22	$-^c$	$-^c$	$-^c$
C_6H_5	2.75	−1.26	−1.32	−1.25	−1.32	−1.40	−1.25
NH_2	2.91	-1.2^d	-1.2^d	−0.90	-1.2^d	-1.2^d	$-^c$
Br	2.96	−1.25	−1.25	−0.85	−1.26	−1.22	−0.90
Cl	3.25	−1.25	−1.23	−0.92	−1.30	−1.28	−0.95
OH	3.43	−1.25	−1.22	−0.85	−1.20	−1.30	−0.87
$OCOCH_3$	3.74	−1.21	−1.21	−0.80	−1.29	−1.30	−0.88

[a] Cavanaugh, J. R.; Dailey, B. P. *J. Chem. Phys.* 1961, *34*, 1099; Fay, C. K. Grutzner, J. B.; Johnson, L. F.; Sternhell, S.; Westerman, P. W. *J. Org. Chem.* 1973, *38*, 3122. [b] All values are in hertz. Accuracy ±0.1 Hz unless specified otherwise. Signs are assumed to be negative. [c] These values were not determined. [d] ±0.2 Hz.

Table IX. Benzylic Coupling Constants of 44d in Various Solvents

solvent	dielec^a const (35 °C)	J_{ob}
acetonitrile	35.8	−1.30
acetone	20	−1.27
dioxane	2.20	−1.29
methylene chloride	8.75	−1.30

[a] Values taken from National Bureau of Standards Circular No. 514, 1951.

in Table VIII. Except for the parent compounds (R = H), the measured values of $J_{ob}(H_a\text{-}H_3)$ and $J_{ob}(H_b\text{-}H_3)$ do not vary by more than 0.2 Hz in Table VIII and are only slightly larger in magnitude than the calculated value.

Substituent and Solvent Dependencies of J_{ob}

Substituent effects on J_{ob} are clearly of importance even though they have not been taken into account in any of the theoretical treatments. As an example, the spread of values for $J_{ob}(60°)$ in Figure 3 cannot be attributed to conformational or "bond order" effects because all geometrical relationships of the type considered give a maximum for the cases in which the benzene ring bisects the benzylic methylene group. However, it can be seen from the data in Table VII that the values for the least ideal dihydrobenzofurans **44** are larger, in fact, than those for the undoubtedly planar fluorenes **45**.

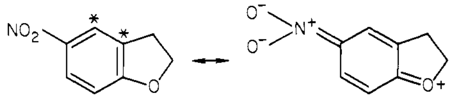
A clear correlation of J_{ob} with substituent electronegativity E_x is to be found for $J_{ob}(H_c\text{-}H_8)$ data for the substituted acenaphthenes **49** and **50** in Table VIII. Linear least-squares fits of the data give

$$J_{ob}(H_c\text{-}H_8) = 0.37E_x - 2.12 \text{ Hz} \tag{11a}$$

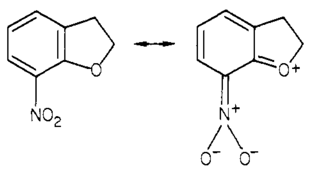
$$J_{ob}(H_c\text{-}H_8) = 0.38E_x - 2.19 \text{ Hz} \tag{11b}$$

for **49** and **50**, respectively, with correlation coefficients $r = 0.91$ and 0.93, respectively. The orthobenzylic coupling constants become more positive with increasing electronegativity. This is consistent with INDO-FPT MO results for allylic coupling on substitution of an electronegative substituent (fluorine) at the C3 carbon atom of propene.[17,43] However, a correlation of cisoid allylic coupling constants with substituent electronegativity was not apparent in the experimental data for C3-substituted propenes.[17] In these cases the coupling constants are averages, which are weighted with respect to the rotamer populations, and these depend, in large measure, on the *size* of the substituent. The most obvious correlation is with the van der Waals radii, and any dependence on electronegativity is obscured.[17]

Orthobenzylic coupling constants in compounds with one or two electronegative substituents on the aromatic ring are identical with J_{ob} for the unsubstituted molecules in the series of 2,3-dihydrobenzofuran derivatives in Table VII. However, J_{ob} for the molecules with nitro groups on the aromatic rings are consistently larger in absolute magnitude. From these results and others obtained in these laboratories, it is noted that the differences are not only consistent but are essentially additive. The results noted for bond fixation in methyl aromatic compounds associated with a pair of a nitro and a hydroxyl group are reflected in the data for the nitro derivatives of 2,3-dihydrobenzofuran. These can be rationalized in terms of the VB structures; J_{ob} would be expected to increase due to the contribution of **51** and **52**, which lead to an increase in the mobile π-bond order between the starred carbon atoms. A similar trend is noted for 5-cyano-2,3-dihydrobenzofuran **44** in Table VII, but the effect is not as pronounced.



51



52

Throughout this work acetone-d_6 was generally used as the solvent for ^1H NMR spectroscopy, except when the compounds reacted with acetone (e.g., amines) or had very poor solubility in this solvent. Acetone-d_6 is known to be a poor solvent for the determination of NMR parameters[44] since it affects chemical shifts although not generally coupling constants.[45] However, for instrumental reasons (it has a strong deuterium resonance which is used as a lock signal and low viscosity) and since only the coupling constants (and not chemical shifts) were of interest in this work, the use of acetone-d_6 as a solvent was justified. To determine if the solvent effect on benzylic coupling constants could indeed be ignored, the ^1H NMR spectra of 5-nitro-2,3-dihydrobenzofuran **44d** were examined in several solvents and the results, together with the values of dielectric constants of each solvent are given in Table IX.

A large amount of experimental data for solvent effects on H–H geminal coupling constants has been obtained in various compounds.[45–47] In most cases the geminal coupling constants decrease in solvents of increasing dielectric constant. The vicinal coupling constant[45] and the coupling constants between protons in aromatic compounds[48] are known to be essentially independent of solvent.

If the dielectric constant of the solvent affects the magnitude of J_{benzylic}, a compound containing two functional groups and showing a bond fixing effect like compound **44d** would be expected to show larger solvent effects than the other compounds in the series. In Table IX J_{ob} varied within 0.03 Hz, which is barely

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(44) Laszlo, P. In Emsley, J. W.; Feeney, J.; Sutcliffe, L. H., Ed. "Progress in Nuclear Magnetic Resonance Spectroscopy", Vol. 3, Pergamon Press: New York, 1967; p 231.

(45) Barfield, M.; Johnston, M. D., Jr. *Chem. Rev.* **1973**, *73*, 53.

(46) Macdonald, C. J.; Schaefer, T. *Can. J. Chem.* **1967**, *45*, 3157.

(47) Smith, S. L.; Ihrig, A. M. *J. Chem. Phys.* **1967**, *46*, 1181.

(48) Castellano, S.; Kostelnik, R.; Sun, C. *Tetrahedron Lett.* **1967**, 4635; Castellano, S.; Sun, C.; Kostelnik, R. *Ibid.* **1967**, 5205; Castellano, S.; Kostelnik, R. *Ibid.* **1967**, 5211.

significant, and showed no trend with dielectric constant. Thus, it appears that solvent effects are not important in those cases in which there are no changes in rotamer populations.[45]

Conclusions

Good correlations of the orthobenzylic coupling constants in methyl aromatic compounds and unsaturated compounds (having vinylic methyl groups) are found with the π-bond order η, the square of η, and the mutual atom–atom polarizability $\pi_{pp'}$. However, the linear dependence on η (which has no theoretical basis) gives values which are much too high in the region of very low bond orders.

In the extension of the study to molecules in which both conformational and bond order effects are important to the J_{ob}, it is found that the generalization of the relationship of coupling constant to $\pi_{pp'}$ to include angular factors gives results which are in very good agreement with the experimental results. The agreement is an improvement on the results based on the INDO-FPT method[34] and is much better than the correlation with η^2. It seems likely that the inadequacy of the latter is due to the overestimation of J^{σ}.

The experimental and theoretical results presented here provide an important method for obtaining useful structural information in complex molecules.

Acknowledgment. This work was supported by Australian Research Grants Committee, Grant C7415407.

Registry No. **1**, 108-88-3; **2**, 115-07-1; **3**, 91-57-6; **4**, 575-41-7; **5**, 581-42-0; **6**, 571-61-9; **7**, 84944-65-0; **8**, 613-26-3; **9**, 782-23-0; **10**, 1576-67-6; **11**, 1576-69-8; **12**, 7372-87-4; **13**, 33982-92-2; **14**, 90-12-0; **15**, 613-12-7; **16**, 883-20-5; **17**, 2871-91-2; **18**, 1705-84-6; **19**, 652-04-0; **20**, 2381-34-2; **21**, 2319-96-2; **22**, 3442-78-2; **23**, 3353-12-6; **24**, 1705-85-7; **25**, 13119-86-3; **26**, 3727-31-9; **27**, 96-39-9; **28**, 767-60-2; **29** (M = H), 768-49-0; **30**, 504-60-9; **31**, 452-68-6; **32**, 14495-51-3; **33** (R = CN), 16955-23-0; **33** (R = COOMe), 84944-66-1; **33** (R = NH_2), 16955-25-2; **33** (R = $NMe_3^+I^-$), 16955-26-3; **33** (R = Cl), 16954-29-3; **33** (R = OH), 2876-02-0; **34**, 99-99-0; **35**, 618-85-9; **36**, 119-33-5; **37a**, 58802-07-6; **37b**, 13771-37-4; **37c**, 13771-38-5; **38**, 84944-67-2; **39**, 33982-90-0; **40**, 84944-68-3; **41**, 13030-26-7; **42a**, 84944-69-4; **42b**, 84944-70-7; **43a**, 84944-71-8; **43b**, 84944-72-9; **43c**, 84944-73-0; **43d**, 84944-74-1; **44a**, 496-16-2; **44b**, 76429-69-1; **44c**, 84944-75-2; **44d**, 17403-47-3; **44e**, 17403-48-4; **44f**, 84944-76-3; **44g**, 84944-77-4; **45a**, 84944-78-5; **45b**, 86-73-7; **45c**, 7012-16-0; **45d**, 58775-05-6; **46**, 85026-14-8; **47**, 15656-90-3; **49** (X = H), 10239-86-8; **49** (X = CH_3), 84959-62-6; **49** (X = $CH(CO_2CH_3)_2$), 84944-79-6; **49** (X = C_6H_5), 84944-80-9; **49** (X = NH_2), 84944-81-0; **49** (X = Br), 84944-82-1; **49** (X = Cl), 84944-83-2; **49** (X = OH), 84944-84-3; **49** (X = $OCOCH_3$), 84944-85-4; **50** (X = H), 4208-97-3; **50** (X = CH_3), 84944-86-5; **50** (X = $CH(CO_2CH_3)_2$), 84944-87-6; **50** (X = C_6H_5), 84944-88-7; **50** (X = NH_2), 84944-89-8; **50** (X = Br), 29094-68-6; **50** (X = Cl), 84944-90-1; **50** (X = OH), 84944-91-2; **50** (X = $OCOCH_3$), 84944-92-3.

Supplementary Material Available: Data concerned with general experimental procedures, synthesis of compounds, and spectral analyses (112 pages). Ordering information is given on any current masthead page.

Mechanism of CO_2 Elimination from Ionized Methyl Haloacetates in the Gas Phase. Formation of $CH_3XCH_2^{+\cdot}$ and $CH_3XCHX^{+\cdot}$ (X = Cl, Br) Halonium Radical Ions

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Abstract: The molecular ions of the methyl esters of chloro-, bromo-, dichloro-, and dibromoacetic acids undergo unimolecular elimination of CO_2 in the gas phase. Collisional activation (CA) mass spectrometry suggests that the resulting $[M - CO_2]^{+\cdot}$ ions possess novel types of hypervalent structures, i.e., $CH_3XCH_2^{+\cdot}$ and $CH_3XCHX^{+\cdot}$ (X = Cl, Br). MNDO and ab initio calculations show that the methylmethylenechloronium radical ion $CH_3ClCH_2^{+\cdot}$ and the isomeric chloroethane cation radical $CH_3CH_2Cl^{+\cdot}$ exist in a potential minimum. MNDO predicts that $CH_3ClCH_2^{+\cdot}$ is more stable than $CH_3CH_2Cl^{+\cdot}$ by 10.1 kcal mol^{-1}, whereas according to 6-31G* and UMP2/6-31G* $CH_3CH_2Cl^{+\cdot}$ is more stable by 9.1 and 6.4 kcal mol^{-1}, respectively. Several possible mechanisms for the dissociative rearrangement $ClCH_2COOCH_3^{+\cdot} \rightarrow CO_2 + CH_3ClCH_2^{+\cdot}$ were investigated computationally by MNDO. Selected intermediates and transition states were also calculated at the 4-31G level. Three competing processes for the unimolecular loss of CO_2 from ionized methyl chloroacetate are examined in detail. According to the calculations the energetically most favorable pathway for the formation of $CH_3ClCH_2^{+\cdot}$ from $ClCH_2COOCH_3^{+\cdot}$ commences with the migration of the ester methyl group to chlorine, followed by the elimination of CO_2 (i.e., $ClCH_2COOCH_3^{+\cdot} \rightarrow H_3CClCH_2COO^{+\cdot} \rightarrow CO_2 + CH_3ClCH_2^{+\cdot}$).

The study of simple molecules in the gas phase often provides an opportunity to generate species that, due to intermolecular reactions, cannot be observed in the condensed phase.[2] This holds in particular for ions, and it is the study of the "isolated" species (e.g., in the gas phase) that allows one to reveal their inherent properties and to study the mechanisms according to which the ions are generated.[3] We shall describe here the results of our combined experimental and theoretical investigation on the electron impact induced CO_2 loss from methyl haloacetates.

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(1) (a) Technion Haifa. (b) Technische Universität Berlin.

(2) The case of the 2-adamantyl cation can be taken as a typical example. The only adamantyl cation detected so far in solution is the 1-adamantyl cation; there is no experimental indication for the existence of 2-adamantyl cation despite a substantial barrier (>30 kcal mol^{-1}) for the isomerization 2-adamantyl → 1-adamantyl cation. In the gas phase, however, both species were recently generated as stable cations and their inherent properties studies. See: (a) Wesdemiotis, C.; Schilling, M.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 950. (b) Houriet, R.; Schwarz, H. *Ibid.* **1979**, *18* 951.

(3) For leading references, see: (a) Williams, D. H. *Acc. Chem. Res.* **1977**, *10*, 280. (b) Bowen, R. D.; Williams, D. H.; Schwarz, H. *Angew, Chem., Int. Ed. Engl.* **1979**, *18*, 451. (c) Arnett, E. M. *Acc. Chem. Res.* **1973**, *6*, 404. (d) Kebarle, P.; Davidson, W. R.; Sunner, J.; Meza-Hajer, S. *Pure Appl. Chem.* **1979**, *51*, 63. (e) Levsen, K. "Fundamental Aspects of Organic Mass Spectrometry"; Verlag Chemie: Weinheim/Bergstrasse, Germany, 1978. (f) Bowers, M. T., Ed. "Gas Phase Ion Chemistry"; Academic Press: New York, 1979.

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