of compounds are similar, and their response to changes in reaction conditions follow comparable trends.

Experimental Section

Cyclopropylacetylene[22] and 1-cyclopropylpropyne[23] were prepared by a didehydrohalogenation procedure.[22] Rates were monitored by UV spectroscopy with Cary 118 and 210 instruments by observation of the decrease of the alkyne or alkene absorption or the increase of the product carbonyl absorption. Gaseous reactants were bubbled into the acid solutions contained in 1-cm UV cells until approximately 3×10^{-3} M solutions were obtained. For liquid substrates, 30 μL of 0.3 M solutions dissolved in MeOH were injected into 3 mL of acid solutions to give 3×10^{-3} M concentrations. The wavelengths of observation were 256 (1- and 2-butyne), 201 (1-butene), 260 (1-hexyne), 202 (3-hexyne), and 218 or 255 nm (1-cyclopropylacetylene). All rates listed are the average of at least two runs (reproducibility ±5%). The absorbance change was generally 0.1 unit.

Formation of ketones from the alkynes according to eq 4 was confirmed by the UV spectra of the products.

Acid molarities were measured by titration of measured volumes. Weight percentages were obtained by titration of weighed samples, and these were used to obtain H_0 and D_0 values.

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. EtC≡CH, 107-00-6; MeC≡CMe, 503-17-3; n-BuC≡CH, 693-02-7; EtCH=CH$_2$, 106-98-9; c-PrC≡CH, 6746-94-7; EtC≡CEt, 928-49-4.

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Electronic Effect of Substituted Methyl Groups (CH$_2$X). Carbon-13 and Fluorine-19 Nuclear Magnetic Resonance Study of Some Benzobicyclo[2.2.2]octen-1-yl Derivatives

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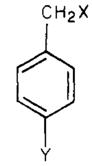
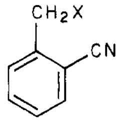
A number of 1-substituted (X) 4-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalenes (**6**), as well as most of their corresponding 6- and 7-fluoro derivatives (**7** and **8**, respectively), have been synthesized and their ^{13}C and ^{19}F NMR spectra have been recorded. The most important feature of these new stereochemically well-defined model benzylic systems is that the CX bond is constrained to the nodal plane of the adjacent aromatic π system; hence, the electronic effect of substituted methyl groups can be assessed in the absence of hyperconjugative interactions involving the CX bond. Linear multiple regression analysis of the ^{13}C SCS of the remote carbon centers in **6** (C6 and C7) and the corresponding ^{19}F SCS of **7** and **8** have been carried out to assess their dependency on substituent parameters (σ_I and $\sigma_R{}^0$). Although the correlations of the former parameters are only fair, the latter parameters provide good to excellent correlations and, moreover, indicate a significant resonance interaction by the substituent (X). The implications of this result with respect to discordant observations concerning the electronic effect of CH$_2$X groups in C$_6$H$_5$CH$_2$X systems is discussed.

There is continued interest in the nature of the electronic effect of substituted methyl groups (CH$_2$X).[1-5] One particular aspect concerns whether or not the conjugative component of the electronic effect of these groups in the neutral ground state is dependent on the resonance capability of the substituent (X). According to the results of multiparameter correlative analyses of ^{13}C[3,6] and ^{19}F[3,7] substituent chemical shifts (SCS; sensitive monitors of π electron effects at remote centers of substituted arene ring systems) as well as infrared frequency shift (ν_{CN} mode)[4] data for the para position of α-substituted toluenes **1–3**, the electronic effect of CH$_2$X groups relative to the methyl substituent (X = H) is predominantly, if not exclusively, determined by the polar nature of the substituent (σ_I effect). The resonance contribution ($\sigma_R{}^0$ effect) has been interpreted as being statistically insignificant.[3]



1, Y = H
2, Y = F
3, Y = CN



4

XCH$_2$CN

5

In contrast, a similar analysis of the cyano frequency shifts (ν_{CN}) of α-substituted *o*-toluonitriles (**4**)[8] and α-substituted acetonitriles (**5**)[4] suggests, besides a polar contribution, a significant dependency of the CH$_2$X electronic effect on the resonance capability of the substituent (X). The origin of the resonance effect was attributed to orbitals on the substituent (X) interacting with the C–H or C–CN σ bonds.[4] Moreover, it was suggested that since this effect can only be significant through space to a nearby probe, the observation of the phenomenon in system **4** but not in **3** is understandable.

We believe the aforementioned apparent discordant experimental observations concerning the electronic effect

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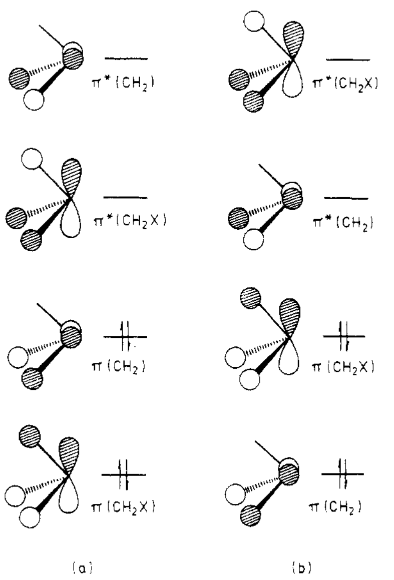
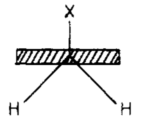
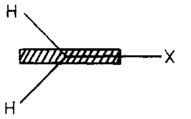


Figure 1. Group orbitals of π symmetry associated with CH_2X substituents: (a) X more electronegative than H, (b) X more electropositive than H.

of CH_2X groups maybe reconciled by qualitative considerations of the properties of the well-known group orbitals of π symmetry associated with these substituents (schematically represented in Figure 1),[1,2,9,10] at the same time taking into account the conformational preference of CH_2X substitutents (rotationally unsymmetrical) with respect to an adjacent π electron substrate. On the basis of purely angular considerations, orbitals of π symmetry located on X will interact with the $\pi(CH_2)$ and $\pi^*(CH_2)$ orbitals (origin of potential $\sigma_R{}^0$ dependency) but not significantly with $\pi(CH_2X)$ and $\pi^*(CH_2X)$ (see Figure 1). Hence, $\sigma_R{}^0$ effects associated with X will be essentially precluded from the benzene ring system in conformation A (C–X bond perpendicular to the benzene ring plane) but maximized in conformation B (C–X bond in the nodal plane of the benzene ring). Since recent conformational studies[11-15] in benzylic systems indicate that the former conformer is preferred over the latter, the absence of a measurable $\sigma_R{}^0$ dependency[3,6,7] in **1**–**3** is therefore not unexpected. Furthermore, the $\sigma_R{}^0$ effect observed in system **4**[4,8] is comprehensible in terms of the proximate cyano probe strongly perturbing the conformational preference of the CH_2X group so that B is now favored over A (coulombic and steric repulsive forces are minimized by X and CN being farthest removed). In model system **5**, the cylindrical symmetry of the cyano probe ensures that the potential $\sigma_R{}^0$ effect of X always remains optimized and, thus, apparently measurable.[4]

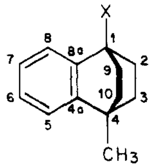


A

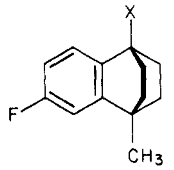


B

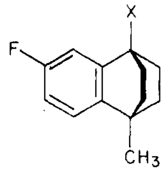
We reasoned that if these suggestions are correct, it should be possible to detect, in a model benzylic system (neutral ground state), the aforementioned $\sigma_R{}^0$ effect of CH_2X groups at remote conjugative positions provided the CX bond is constrained to the nodal plane of the benzene ring so that the appropriate resonance interaction is optimized. Although no such model system is possible when the benzylic carbon center is attached to two hydrogen atoms, an alternative is one in which the benzylic CH bonds are replaced by CC bonds, namely, the benzobicyclo[2.2.2]octen-1-yl skeletal framework.[16] Therefore, in order to test our proposals (vide supra), we have synthesized a number of 1-substituted 4-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalenes (**6**), as well as their corresponding 6- and 7-fluoro derivatives (**7** and **8**, respectively), and measured their ^{13}C and ^{19}F NMR spectra.



6



7



8

The number of compounds prepared was essentially determined by the stipulation[18] concerning the minimal basis set of substituents required in order to effect meaningful multiparameter correlative analysis of physicochemical data.

The most important feature of the stereochemically well-defined model benzylic systems (**6**–**8**) is that the CX bond is constrained to the nodal plane of the adjacent aromatic π system; thus, the potential resonance effect of the substituent (X) is optimized and, moreover, can be assessed at remote positions of the arene ring [C(6) and C(7); conjugated and unconjugated, respectively, with respect to X] in the complete absence of hyperconjugative interactions involving the CX σ bond. The latter effect is an additional complication to contend with in the study of mobile benzylic systems (**1**–**4**). Since the orbital energies and overlap integrals[19] governing the possible $\sigma_R{}^0$ effect should not be vastly disparate for CC vs. CH bonds,[20] it should be valid to extrapolate conclusions drawn from the study of **6**–**8** to CH_2X groups.

Herein we report the results of our investigation.

Results and Discussion

Synthesis of Compounds. The preparations of 1-methoxy-4-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (**6**, X = OMe), 4-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalen-1-ol (**6**, X = OH), and 1-fluoro-4-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (**6**, X = F) have been presented elsewhere[21] in connection with other studies.[12,17] Further functionalization at the bridgehead of the benzobicyclo[2.2.2]octen-1-yl skeletal

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(20) The fact that the hyperconjugating abilities of CC and CH bonds are almost indistinguishable in the neutral ground state is supportive of this point.

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Table I. ^{13}C Substituent Chemical Shifts (SCS)[a,b] of 1-Substituted 4-Methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalenes (6)

	substituent chemical shift[e]										
X	C1	C2	C3	C4	C5	C6	C7	C8	C8a	C4a	CH_3
					$DCCl_3$[c]						
NO_2	54.61	4.05	−0.19	0.65	0.63	2.02	0.93	−3.64	−6.46	−2.60	−0.73
CN	1.47	4.66	−0.93	−0.15	0.63	1.98	0.91	−1.32	−7.11	−2.45	−0.36
COOH	12.53	2.60	−0.37	0.52	0.48	0.89	0.33	−1.37	−3.88	−1.13	−0.06
$CONH_2$	NO	2.97	−0.15	0.48	0.50	0.83	0.43	−1.19	−3.04	−0.80	−0.10
$COOCH_3$	12.66	2.60	−0.28	0.46	0.39	0.74	0.20	−1.47	−3.08	−1.02	−0.08
F	60.31	4.82	0.31	−0.02	−0.14	0.85	0.41	−4.85	−2.45	−3.12	−0.85
Cl	34.48	10.73	1.59	−0.04	−0.12	1.29	0.62	−1.40	−2.34	−1.89	−0.37
Br	31.07	12.24	2.45	−0.26	−0.26	1.50	0.74	1.21	−2.34	−1.82	−0.28
I	15.08	15.62	3.56	−0.60	−0.43	1.87	1.00	5.94	−1.65	−2.13	0.03
NH_2	17.73	8.75	0.76	NO	−0.09	0.24	0.20	−4.25	1.32	−1.41	−0.13
OH	37.77	7.67	0.65	NO	−0.15	0.44	0.28	−4.57	0.34	−2.30	−0.47
OCH_3	41.84	2.93	0.48	−0.30	−0.01	0.25	0.09	−3.28	−1.05	−1.80	−0.41
CH_3	0.04	7.47	0.93	0.26	−0.15	−0.21	−0.04	−2.75	1.95	−0.13	0.24
$Sn(CH_3)_3$	−1.63	3.90	1.48	−0.24	0.41	0.00	−0.02	1.78	2.47	2.42	0.40
					CF_3COOH[d]						
NH_3^+	23.47	4.57	−0.85	0.00	1.26	2.88	0.80	−6.63	−9.40	−3.10	−0.99

[a] Defined as the difference (in parts per million) between the ^{13}C chemical shift of the substituted compound and that of the appropriate carbon in the parent hydrocarbon (X = H). Positive values indicate decreased shielding. The carbon numbering system is as shown on the structural formula **6**. [b] Accurate to ±0.04 ppm. [c] X = H ($DCCl_3$, relative to Me_4Si): 34.65 (C1), 27.11 (C2), 33.65 (C3), 34.43 (C4), 120.68 (C5), 125.68 (C6), 125.51 (C7), 123.28 (C8), 144.15 (C8a), 146.23 (C4a), 23.03 ppm (CH_3). [d] X = H (CF_3CO_2H, relative to Me_4Si): 36.64 (C1), 28.41 (C2), 35.02 (C3), 35.99 (C4), 122.52 (C5), 127.38 (C6), 127.16 (C7), 125.12 (C8), 146.96 (C8a), 148.98 (C4a), 23.53 ppm (CH_3). [e] NO = not observed.

Table II. ^{13}C Substituent Chemical Shifts (SCS)[a,b] of Arene Ring Carbons of System 6 in Cyclohexane[c]

	substituent chemical shift					
X	C5	C6	C7	C8	C8a	C4a
NO_2	0.38	1.62	0.83	−3.02	−5.45	−2.25
CN	0.47	1.69	0.90	−0.90	−5.91	−2.14
COOH	0.33	0.67	0.23	−0.94	−3.20	−0.92
$COOCH_3$	0.18	0.41	0.05	−0.98	−2.35	−0.79
F	−0.31	0.61	0.35	−4.49	−1.64	−2.96
Br	−0.44	1.24	0.70	1.69	−1.67	−1.66
I	−0.58	1.62	0.97	6.47	−0.97	−2.00
NH_2	−0.34	−0.11	0.05	−3.72	2.27	−1.32
OH	−0.40	0.10	0.14	−3.80	1.15	−2.16
OCH_3	−0.08	−0.06	−0.06	−3.03	−0.24	−1.90
CH_3	−0.16	−0.28	−0.03	−2.83	1.89	−0.12

[a] See footnote *a* to Table I. [b] Accurate to ±0.02 ppm. [c] X = H (c-C_6H_{12}, relative to internal benzene): −7.62 (C5), −2.26 (C6), −2.51 (C7), −4.95 (C8), 15.48 (C8a), 17.49 ppm (C4a).

framework hinged on the development of a successful procedure for the conversion of either the methoxy or hydroxy precursors (**6**, X = OMe or OH) to a halogen derivative (**6**, X = Br or I), which can be manipulated in an appropriate manner. Our previous attempts[21] to replace OMe and OH with F in this system suggested that transformations at the bridgehead involving carbonium ions as intermediates may be a problem. Hence, it was not surprising to find that the methoxy and hydroxy compounds proved to be relatively inert toward reagents (acetyl halides and thionyl halides, respectively, in the presence of Lewis acids) which have been successfully employed in the bridgehead transformations of hydroxy- and methoxybicyclo[2.2.2]octanes.[22,23] Apparently benzo annelation of the bicyclo[2.2.2]octane ring precludes the skeletal framework from undergoing the necessary structural adjustment required to generate sufficient carbonium ion stability at the bridgehead position.[24] However, it should be noted that the bridgehead bromide (**6**, X = Br) was obtained in very low yield on treatment of the alcohol (**6**, X = OH) with excess phosphorous tribromide and polyphosphoric acid. The corresponding chloride (**6**, X = Cl) was obtained serendipitously as a minor product from an attempt to acetylate the fluoro derivative (**6**, X = F)[21] on treatment with acetyl chloride/$AlCl_3$.

An efficient conversion of the alcohol (**6**, X = OH) to the iodide (**6**, X = I) was finally achieved via the chloroformate derivative (**6**, X = OCOCl) which, when placed under reflux with excess sodium iodide in acetone, afforded the iodide (**6**, X = I) in respectable yields. The success of this reaction can be attributed to the fact that a bridgehead radical rather than a carbonium ion mediates the transformation. The iodide (**6**, X = I) served as the crucial precursor for the synthesis of a number of other bridgehead-substituted derivatives by well-established literature procedures. The preparation of one of these, 1-(trimethylstannyl)-4-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (**6**, X = $SnMe_3$), has already been described.[15]

Except for the bridgehead fluoro derivatives of systems **7** and **8** (X = F), which were available as a mixture from a previous study,[17,21] the starting point for the synthesis of these systems was the methoxy precursor (**6**, X = OMe). Nitration of this compound afforded a mixture of the 6- and 7-*mononitro* derivatives in a ratio of 1:2 (GLC). The nitro mixture was hydrogenated to give the corresponding amines which were converted via the diazonium hexafluorophosphates to an isomeric mixture of 6- and 7-fluoro-1-methoxy-4-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (**7** and **8**, respectively; X = OMe). These were then converted to a mixture of the hydroxy compounds (**7** and **8**, X = OH) and then to various other bridgehead substituent mixtures (**7** and **8**) by using functionalization procedures similar to those employed for the synthesis of bridgehead derivatives of system **6**. It is important to note that separation of the various isomeric mixtures of **7** and **8** (never 1:1) was not necessary since isomer identification was unambiguously established for each mixture by ^{13}C NMR (the 7 isomer (system **8**) was always dominant).[25]

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Table III. ^{19}F Substituent Chemical Shifts (SCS)[a,b] of Systems 7 and 8

X	substituent chemical shift					
	cyclohexane		$DCCl_3$		DMF	
	7[c]	8[d]	7	8	7	8
NO_2	2.85	3.02	3.29	3.01	2.87	2.24
CN	2.83	2.81	3.18	2.68	2.71	1.95
COOH	1.25	1.52	1.51	1.47	0.76	0.67
$CONH_2$			1.39	1.64	0.32	0.44
$COOCH_3$	0.78	1.11	1.25	1.23		
F	0.90	1.86	1.17	1.83	1.13	1.53
I	1.31	1.98	1.55	1.84	1.50	1.45
NH_2[d]	−0.60	0.89	0.07	1.21	−0.91	0.43
OH[e,f]	−0.11	1.25	0.34	1.44	−0.68	0.54
OCH_3	−0.40	0.89	0.08	1.09	−0.16	0.77
CH_3[g]	−0.61	0.47	−0.55	0.46	−0.55	0.51
$Sn(CH_3)_3$	0.00	0.25	0.12	0.34		

[a] Defined as the difference (in parts per million) between the ^{19}F chemical shift of the substituted compound and that of the parent compound (X = H). A positive sign implies deshielding. [b] Accurate to ±0.01 ppm. [c] X = H (relative to internal $FCCl_3$), −116.74 ppm; X = H (relative to internal fluorobenzene), −4.05 ppm. [d] X = H (relative to internal $FCCl_3$), −117.81 ppm; X = H (relative to internal fluorobenzene), −5.12 ppm. [d] NH_3^+ (CF_3CO_2H, systems 7 and 8), 5.21 and 3.88 ppm, respectively. [e] OH (HMPA, systems 7 and 8), −1.20 and 0.00 ppm, respectively. [f] O^-K^+ (HMPA, systems 7 and 8), −5.55 and − 0.15 ppm, respectively. [g] CH_3 (CF_3CO_2H, systems 7 and 8), −0.56 and 0.50 ppm, respectively.

^{13}C and ^{19}F NMR Spectra. The ^{13}C substituent chemical shift (SCS) data for system 6 in $DCCl_3$ and c-C_6H_{12} are tabulated in Tables I and II, respectively. The chemical shifts ($DCCl_3$, relative to Me_4Si) of three of these compounds (X = H, F, and $SnMe_3$) have been previously reported in connection with other studies.[12,15] Assignments followed unambiguously from the application of various routine techniques such as chemical shift, intensity, off-resonance noise decoupling, and substituent effect considerations as well as the "fluoro substitution" technique.[26,27] The latter, based on the ^{13}C NMR spectra of the mixtures of 7 and 8,[25] proved indispensable for distinguishing between C6 and C7.

Table III gives the ^{19}F SCS for systems 7 and 8 in various solvents.

Correlative Analyses. It is now well established that the utilization of ^{13}C and ^{19}F SCS values as sensitive π charge density probes[28,29] must be confined to sites remote from the point of substitution such that the manifold of other likely determining factors (steric, magnetic anisotropic, bond order, and neighboring group effects) is unimportant. Hence, in system 6 the appropriate carbon centers for monitoring the electronic effects of X by ^{13}C and ^{19}F NMR are C6 and C7 (formally para and meta dispositions, respectively, with respect to X). By the use of linear multiple regression analysis, we have explored the relationship between the ^{13}C SCS of these remote carbon centers (C6 and C7; Tables I and II) and substituent pa-

Table IV. Results of Correlative Analysis[a] of ^{13}C SCS Values of System 6 with Substituent Parameters

carbon center	solvent	independent variables	ρ_I[b]	ρ_R[b]	c[c]	r[d]	SE[e]	F[f]	F_I[f]	F_R[f]	n[g]
C6	c-C_6H_{12}	σ_I	3.45 ± 0.47		−0.41	0.924	0.30	52.90[h]	52.90[h]		11
C6	c-C_6H_{12}	σ_I, σ_R^0	3.12 ± 0.56	0.54 ± 0.49	−0.22	0.935	0.30	27.65[i]	31.52[i]	1.204[j]	11
C7	c-C_6H_{12}	σ_I	1.76 ± 0.30		−0.18	0.890	0.19	34.23[i]	34.23[i]		11
C7	c-C_6H_{12}	σ_I	1.64 ± 0.21		−0.19	0.941	0.13	62.19[h]	62.19[h]		10[n]
C7	c-C_6H_{12}	σ_I, σ_R^0	1.57 ± 0.26	0.11 ± 0.23	−0.15	0.943	0.14	28.30[i]	36.36[i]	0.25[k]	10[n]
C6	$DCCl_3$	σ_I	3.68 ± 0.46		−0.29	0.923	0.31	63.63[h]	63.63[h]		13
C6	$DCCl_3$	σ_I, σ_R^0	3.47 ± 0.41	0.81 ± 0.39	−0.09	0.948	0.27	43.93[h]	70.52[l]	4.43[l]	13
C7	$DCCl_3$	σ_I	1.71 ± 0.26		−0.12	0.894	0.17	44.00[h]	44.00		13
C7	$DCCl_3$	σ_I	1.61 ± 0.18		−0.13	0.943	0.12	79.73[h]	79.73[h]		12[n]
C7	$DCCl_3$	σ_I, σ_R^0	1.56 ± 0.18	0.21 ± 0.17	−0.08	0.951	0.12	42.70[h]	74.23[h]	1.52[m]	12[n]

[a] General form of correlation equation: $SCS = \rho_I\sigma_I + \rho_R\sigma_R^0 + c$. [b] Regression coefficients for individual terms ± standard error of regression coefficient. [c] Intercept. [d] Multiple correlation coefficient. [e] Standard error of estimate. [f] F test of variance for overall correlation and individual regression coefficients. Superscripts indicate confidence level (CL) of test. [g] Number of data points in correlation. [h] 99.99% CL. [i] 99.9% CL. [j] 70.0% CL. [k] 37.0% CL. [l] 94% CL. [m] 75% CL. [n] SCS of I omitted from data set.

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(25) (a) Full details of the ^{13}C NMR spectra of these mixtures (7 and 8) may be found elsewhere.[21,25b] (b) Abeywickrema, A. N. Ph.D. Dissertation, The Flinders University of South Australia, 1981.

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(27) Adcock, W.; Gupta, B. D.; Kitching, W. *J. Org. Chem.* **1976**, *41*, 1498.

(28) Hehre, W. J.; Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* **1976**, *12*, 159 and references cited therein.

(29) (a) Martin, G. J.; Martin, M. L.; Odiot, S. *Org. Magn. Reson.* **1975**, *7*, 2 and references cited therein. (b) Nelson, G. L.; William E. A. *Prog. Phys. Org. Chem.* **1976**, *12*, 229 and references cited therein.

rameters (σ_I and σ_R^0),[30,31] which are known to characterize electric field and resonance effects, respectively.[32] Similar correlations were also carried out on the corresponding ^{19}F SCS (systems 7 and 8; Table III). The regression parameters for the various correlations are set out in Tables IV and V.

An inspection of these results brings to light several significant features. First, it can be seen that the statistical fits of the ^{13}C SCS correlations (Table IV) are barely acceptable[33] for both carbon centers. Significantly, the inclusion of σ_R^0 in the correlations, particularly for C6 (conjugated), does not lead to any statistically significant improvement in the fit (note that the *F* test of the variance actually decreases for C6 and C7 in both solvents).[34] Clearly, the only conclusion to be drawn from these linear trends is that there is a reasonably strong relationship between the ^{13}C SCS (C6 and C7) and σ_I parameters. This was to be expected since the structural constraints inherent in the model system are such that π electron charge redistribution at remote centers is determined essentially by the electric field of the dipolar substituent at the bridgehead position [field-induced π polarization (F_π); σ_I effect].[30c,35,36] Although the less than perfect fits for the correlations may be due, in part, to the small range of shifts (particularly for C7), other factors may also be slightly perturbing the ^{13}C chemical shifts. An examination of molecular models of system 6 indicates considerable "perilike" steric buttressing interactions between C1–X and C8–H; hence, substituent-induced skeletal distortion of the aromatic ring is a possible perturbation. However, the insignificant SCS values for the nonpolar CH_3 and $SnMe_3$ groups ($\sigma_I = 0.00$)[37,38] at C7 (Table I) offers no support for this idea. Another possible minor factor could be σ charge density perturbations[39] at C6 and C7 due to electronic interactions involving the σ-bonded framework.[40]

Second, it can be seen (Table V) that the precision of fits for the ^{19}F SCS correlations range from good to ex-

Table V. Results of Correlative Analysis[a] of ^{19}F SCS of Systems 7 and 8 with Substituent Parameters

system	solvent	independent variables	ρ_I[b]	ρ_R[b]	c[c]	r[d]	SE[e]	F[f]	F_I[f]	F_R[f]	n[g]
7	$c\text{-}C_6H_{12}$	σ_I	5.23 ± 0.80		−0.70	0.908	0.55	42.40[h]	42.40[h]		11
7	$c\text{-}C_6H_{12}$	σ_I, σ_R^0	4.38 ± 0.52	2.02 ± 0.48	−0.16	0.972	0.33	69.71[h]	72.04[h]	17.81[i]	11
7	$c\text{-}C_6H_{12}$	σ_I, σ_R^0	4.46 ± 0.31	2.00 ± 0.28	−0.26	0.991	0.19	201.8[h]	211.6[h]	49.49[j]	10[o]
7	$DCCl_3$	σ_I, σ_R^0	5.13 ± 0.44	2.06 ± 0.40	−0.19	0.983	0.28	101.2[h]	134.6[h]	26.49[j]	10[o]
7	DMF	σ_I, σ_R^0	5.13 ± 0.67	2.40 ± 0.62	−0.19	0.985	0.29	95.60[h]	58.67[j]	14.81[k]	9
8	$c\text{-}C_6H_{12}$	σ_I	4.06 ± 0.20		0.33	0.989	0.14	417.8[h]	417.8[h]		11
8	$c\text{-}C_6H_{12}$	σ_I, σ_R^0	4.04 ± 0.23	0.06 ± 0.21	0.35	0.989	0.14	187.3[h]	313.3[h]	0.07[l]	11
8	$DCCl_3$	σ_I	3.94 ± 0.24		0.30	0.984	0.15	281.1[h]	281.1[h]		11
8	$DCCl_3$	σ_I, σ_R^0	3.90 ± 0.25	0.18 ± 0.22	0.35	0.986	0.15	135.9[h]	248.6[h]	0.68[m]	11
8	DMF	σ_I	3.32 ± 0.32		0.19	0.970	0.18	110.7[h]	110.7[h]		9
8	DMF	σ_I, σ_R^0	2.90 ± 0.36	0.61 ± 0.33	0.43	0.981	0.15	75.24[h]	65.49[j]	3.31[n]	9

[a] General form of correlation equation: $SCS = \rho_I\sigma_I + \rho_R\sigma_R^0 + c$. [b] Regression coefficients for individual terms ± standard error of regression coefficient. [c] Intercept. [d] Multiple correlation coefficient. [e] Standard error of estimate. [f] *F* test of variance for overall correlation and individual regression coefficients. Superscripts indicate confidence level (CL) of test. [g] Number of data points in correlation. [h] 99.99% CL. [i] 99.7% CL. [j] 99.9% CL. [k] 99.1% CL. [l] 20% CL. [m] 57% CL. [n] 88% CL. [o] SCS of COOH omitted from data set.

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(30) (a) In order to avoid likely solvent discrepancies in the known σ_I values of substituents[18,30b] and, in addition, to avoid using statistically refined values which may not be strictly applicable to model systems where the substituent is directly attached to an sp^3-hybridized carbon atom, we have employed new σ_I scales for each solvent. These were derived from the ^{19}F SCS of 1-substituted 4-(*p*-fluorophenyl)bicyclo[2.2.2]octanes[30c] in the appropriate solvent. Since solvent effect studies have shown that Br is a "chemically" inert substituent,[30d] scaling was achieved by setting σ_I for this substituent equal to 0.44[30b] for each solvent. A tabulation of these new σ_I scales will be published in connection with other studies.[30e] (b) Bromilow, J.; Brownlee, R. T. C.; Lopez, V. O.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 4766. (c) Adcock, W.; Khor, T. C. *J. Am. Chem. Soc.* **1978**, *100*, 7799. (d) Taft, R. W.; Price, E.; Fox, I. R.; Lewis, I. C.; Andersen, K. K.; Davis, G. T. *Ibid.* **1963**, *85*, 709, 3146. (e) Adcock, W.; Abeywickrema, A. N., to be submitted to *J. Org. Chem.*

(31) Since the conjugative effect of a substituent is a function of the reference substrate, it may be argued that σ_R^0 values, which are, strictly speaking, measures of the resonance effects of substituents directly attached to a benzene ring system,[30b] are not applicable to aliphatic substrates. However, provided the substituents making up the basis set are either donor or acceptor dominant, it seems reasonable to assume that the relative magnitude of their resonance effects should be independent of the nature of the substrate.

(32) Reynolds, W. F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 985 and references cited therein.

(33) Davis, W. H.; Pryor, W. A. *J. Chem. Educ.* **1976**, *53*, 285.

(34) A larger value of *F* implies a better overall correlation or a greater significance of an individual regression coefficient.

(35) Reynolds, W. F.; Hamer, G. K. *J. Am. Chem. Soc.* **1976**, *98*, 7296 and references cited therein.

(36) Adcock, W.; Cox, D. P. *J. Org. Chem.* **1979**, *44*, 3004 and references cited therein.

(37) Adcock, W.; Khor, T. C. *J. Org. Chem.* **1978**, *43*, 1272.

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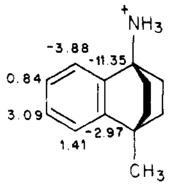
(39) Seidman, K.; Maciel, G. E. *J. Am. Chem. Soc.* **1977**, *99*, 3254.

(40) Eliel, E. L.; Bailey, W. F.; Kopp, L. D.; Miller, R. L.; Grant, D. M.; Bertrand, R.; Christensen, K. A.; Dalling, D. K.; Duch, M. W.; Wenkert, E.; Schell, F. M.; Cochran, D. W. *J. Am. Chem. Soc.* **1975**, *97*, 322.

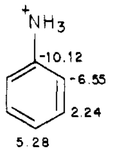
cellent, indicating that they reflect predominantly π electronic perturbations induced by the substituent. These results stand in striking contrast to those mentioned above for the corresponding ^{13}C SCS. Although we have no explanation for this apparent discrepancy, it should be noted that other instances have been reported[41] where ^{19}F SCS appear to be more reliable probes of substituent-induced π electron effects than the corresponding ^{13}C SCS. However, the most noteworthy feature of the ^{19}F SCS correlations (Table V) is that the inclusion of $\sigma_R{}^0$ in the correlations of system 7 (conjugated) for all solvents, but not those of system 8 (unconjugated), leads to a statistically significant improvement in the fit.[34] Hence, we believe compelling experimental evidence is provided for the fact that the resonance effect of X contributes significantly to the potential conjugative interactions of substituted alkyl groups. In this connection, it is of interest to note that Wiberg[42] has presented ab initio molecular orbital calculations on CH_3X derivatives which suggest a significant resonance effect between the substituent (X) and the CH bonds. The failure to detect this weak $\sigma_R{}^0$ effect of CH_2X substituents in $C_6H_5CH_2X$ systems **1–3** must therefore be associated with its conformational dependency (see beginning of paper). The recognition of this hitherto unrealized phenomenon allows a number of apparent discordant observations concerning the electronic effect of this group to be reconciled.

A comparison of the polar susceptibility parameter (ρ_I value) for systems **7** [$\rho_I = 4.46$ (c-C_6H_{12}); Table V] and **2** [$\rho_I = 10.51$ (CCl_4)][7] is of interest since the substituent and fluorine in both substrates are similarly disposed (para). Moreover, although the CH_2X group is conformationally mobile in the latter system, the angle and distance relationships determining the magnitude of the polar field effect (direct field and F_π effects)[30c,35,36] are similar for both systems. Hence, on the basis of the usual assumption that ρ_I is a manifestation of only polar field effects, ρ_I values of comparable magnitude were expected for **7** and **2**. Note, however, that the value for **2** is more than twice as large as that observed for **7**. This is a highly significant result which we believe is indicative of an additional contribution, besides polar field effects, to the ρ_I value for system **2**. It is important to note that Taft et al.[7] reached a similar conclusion based on a comparison of the ρ_I value for **2** with that observed for the p-XC_6H_4F system [$\rho_I = 7.03$ (c-C_6H_{12})]. These workers ascribed the additional contribution to ρ_I of **2** to the polar effect of X on no-bond resonance forms involving the CH bond. However, the comparison in this study implicates, unambiguously, hyperconjugation involving the CX rather than the CH bond(s). It follows, then, that σ–π interactions involving the CX bond in $C_6H_5CH_2X$ systems **1–3** contribute significantly to the overall π-electron perturbation at the conjugated para position.[43] In contrast, Shapiro[6b] has concluded otherwise on the basis of the premise that hyperconjugative interactions should be manifest in the resonance susceptibility term (ρ_R). It is our belief that the unambiguous dissection of the electronic effect of CH_2X groups into polar field and resonance components by regression analysis requires treating these substituents as whole moieties.[44]

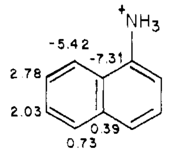
Finally, we would like to draw attention to the aryl ^{13}C SCS of system **6** (Table I) for the ammonio ($^+NH_3$) substituent relative to those for CH_3 as a reference. These are set out on structure **9** to facilitate comparison with the corresponding shift for monosubstituted benzene (**10**)[36] and 1-substituted naphthalene (**11**).[36] Previous studies[35,36] of various ring systems (benzene, biphenyl, and naphthalene) have shown that the comparison of ^{13}C chemical shifts of these isoelectronic substituents minimize steric and resonance factors and, hence, provide a qualitative indication of the π polarization pattern induced by the electric field of the positive charge. It can be seen (compare **9** and **10**) that the pattern of polarization in the benzene ring of system **6** is very similar to that observed in the anilinium ion.[45] The major differences, particularly those at the remote meta and para positions, may be ascribed to the orientation dependence of the effect.[27,35] Most importantly, however, the polarization pattern of system **6** is quite different from that observed for the similarly disposed ring of 1-substituted naphthalene (compare **9** and **11**). This result highlights the inadequacies of a simple bond polarizability model for describing electric field induced π polarization influences, an important mode of transmission of polar effects in aryl systems. An appropriate model, therefore, must view the π system as being polarized as a whole.[46]



9



10



11

Experimental Section

The standard functionalizing procedures employed for preparing the substituted derivatives of system **6**, together with yields and physical properties, are listed in Table VI.

1-Iodo-4-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (6, X = I). A solution of **6** (X = OH;[21] 18.8 g, 0.1 mol) and pyridine (13.0 g, 0.16 mol) in benzene (500 mL) was added over a period of 1 h to a stirred solution of phosgene (60 g, 0.91 mol) in benzene (200 mL) maintained below 4 °C.[47] The resulting white slurry was stirred at the same temperature for 30 min and allowed to warm to room temperature. After the mixture was allowed to stand for 1 h, the precipitate was removed by filtration and the filtrate washed with ice–water (2 × 500 mL). Drying and removal of the solvent gave the chloroformate **6** (X = OCOCl; 24.0 g, 96%) as a pale yellow liquid which solidified on standing.

A stirred slurry of **6** (X = OCOCl; 24.0 g, 0.096 mol) and anhydrous sodium iodide (200 g, 1.33 mol) in dry acetone (500 mL) was heated under reflux for 12 h.[48] After removal of most of the solvent by distillation, the crude dark residue was poured onto water and then extracted with ether (three times). The combined extracts were washed with a solution of sodium thiosulfate and dried, and the solvent, as well as the low boiling products, was evaporated under vacuum. Analysis of the crude residue by VPC indicated the presence of the required iodide (**6**,

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[41] (a) The conjugated 8-position in 2-substituted naphthalenes[41b] and the α- and β-positions in the aromatic ring of benzocycloalkenes.[41c] (b) Kitching, W.; Bullpitt, M.; Gartshore, D.; Adcock, W.; Khor, T. C.; Doddrell, D.; Rae, I. D. *J. Org. Chem.* **1977**, *42*, 2411. (c) Adcock, W.; Gupta, B. D.; Khor, T. C. *Aust. J. Chem.* **1976**, *29*, 2571.

[42] Wiberg, K. B. *J. Am. Chem. Soc.* **1979**, *101*, 2204; **1980**, *102*, 1229.

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[45] (a) It is of interest to note that the ^{13}C SCS (relative to CH_3) of $^+NH_3$ for C6 in system **6** is substantially less than the corresponding para ^{13}C SCS (5.01 ppm) of benzylammonium trifluoroacetate.[45b] Thus, hyperconjugative electron withdrawal involving the C–N bond is implicated in the latter system.[45c] (b) Reynolds, W. F.; Peat, I. R.; Freedman, M. H.; Lyerla, J. R. *Can. J. Chem.* **1973**, *51*, 1857. (c) Adcock, W.; Alste, J.; Rizvi, S. Q. A.; Aurangzeb, M. *J. Am. Chem. Soc.* **1976**, *98*, 1701.

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Table VI. Synthetic Methods, Yields, and Melting (or Boiling) Points of 1-Substituted 4-Methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalenes (6)[a,b]

X	precursor (quantity)	synthetic method	% yield	mp or bp, °C
H	I (1.5 g, 0.005 mol)[c]	(1) *t*-BuLi (0.008 mol)/Et_2O/–80 °C, (2) CH_3OH/H_2O/–80 °C	88	60–65 (2 mm)[j] [$n^{24}{}_D$ 1.5475]
COOH	I (6.0 g, 0.02 mol)	(1) *t*-BuLi (0.03 mol)/Et_2O/–80 °C, (2) CO_2/–80 °C	88	157.5–158.5[k]
$COOCH_3$	COOH	CH_2N_2/Et_2O[d]	95	73–74[l]
$CONH_2$	COOH (2.16 g, 0.01 mol)	$SOCl_2/NH_3$	98	217–218[m]
CN	$CONH_2$ (0.86 g, 0.004 mol)	$(CF_3CO)_2O$/pyridine[e]	89	85–90 (0.1 mm)[j] [$n^{18}{}_D$ 1.5475]
NH_2	COOH (2.16 g, 0.01 mol)	(1) $SOCl_2$, (2) NaN_3, (3) Curtius reaction conditions[f]	77	65–70 (0.2 mm)[j]
NO_2	NH_2 (1.12 g, 0.006 mol)	$KMnO_4/MgSO_4$·[g]	54	63–64[l]
CH_3	COOH (1.1 g, 0.005 mol)	(1) $LiAlH_4$, (2) Ph_3P/CCl_4[h] (3) Mg/THF, (4) NH_4Cl/H_2O	20	75–80 (0.5 mm)[j]
Cl	F (1.5 g, 0.008 mol)	$CH_3COCl/AlCl_3$	5	80–85 (0.5 mm)[j]
Br	OH (1.5 g, 0.008 mol)	PBr_3/H_3PO_4/140 °C[i]	10	85–90 (0.1 mm)[j]

[a] The proton and carbon-13 (see Table II) NMR and mass spectra were clearly in accord with the assigned structures.

[b] The elemental analyses agreed well with those calculated (C, ±0.3; H, ±0.2).

[c] This study.

[d] Vogel, A. I. "Practical Organic Chemistry"; Longmans: London, 1970; pp 971–973.

[e] Campagna, F.; Carrotti, A.; Casini, G. *Tetrahedron Lett.* **1977**, 1813.

[f] Smith, P. A. S. *Org. React.* **1947**, *3*, 337.

[g] Kornblum, N.; Jones, W. J. *Org. Synth.* **1963**, *43*, 87.

[h] Brett, D.; Downie, J. M.; Lee, J. B. *J. Org. Chem.* **1967**, *32*, 855.

[i] Kopecký, J.; Smejkal, J. *Tetrahedron Lett.* **1967**, 1931.

[j] Colorless oils.

[k] Recrystallized from hexane/ethanol as colorless prisms.

[l] Recrystallized from ethanol/water as colorless needles.

[m] Recrystallized from hexane/ethanol as colorless flakes.

X = I) and the starting alcohol (6, X = OH) as the major products in approximately equal amounts. The mixture was chromatographed on a silica gel column. Elution with pentane gave a yellow oil which, on distillation, afforded 6 (X = I; 11.7 g, 41%) as a colorless liquid: bp 103–105 °C (0.1 mm); mass spectrum, *m/e* 298 (M^+). Anal. ($C_{13}H_{15}I$) C, H. Elution with ether, followed by recrystallization and sublimation, gave 6 (X = OH): 7.0 g (37%); mp 101.5 °C (lit.[21] mp 101.5 °C).

It is of interest to note that the formation of the iodide and the alcohol in similar yields suggests that the intermediate iodoformate decomposes by two distinct and equally probable pathways: one involving alkyl–oxygen bond fission (–CO_2) and the other acyl–oxygen bond fission (–CO).

Preparation of Mixtures of 7 and 8. 1-Methoxy-4-methyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (6, X = OCH_3) was nitrated according to a method outlined by Tanida and Muneyuki[49] to afford a mixture of the 6- and 7-nitro derivatives of 6 (X = OCH_3): 93% yield; bp 120–125 °C (0.1 mm). This mixture was catalytically reduced and then converted to the diazonium hexafluorophosphate salts (mp 100–101 °C dec) according to a method outlined by Rutherford and Redmond.[50] The dry powdered diazonium salt was decomposed by portionwise addition to hot (120–125 °C) mineral oil. Steam distillation followed by distillation [bp 106–110 °C (0.1 mm)] gave the mixture of 6- and 7-fluoro derivatives of 6 (X = OCH_3) as a colorless oil (55% yield). This mixture, when treated with HBr and acetic anhydride as previously described for the preparation of 6 (X = OH),[21] afforded a mixture of the bridgehead alcohols 7 and 8 (X = OH) in good yield (92%). These were then converted to a mixture of the iodo compounds 7 and 8 (X = I) by using the procedure described above for the synthesis of 6 (X = I). Column chromatography followed by distillation [bp 95–100 °C (0.05 mm)] afforded the iodo mixture in good yield (40%). Further functionalization was achieved according to the synthetic methods listed in Table VI for the bridgehead derivatives of 6. A mixture of the $Sn(CH_3)_3$ derivatives (7 and 8, X = $SnMe_3$) was obtained by treatment of the iodo mixture with trimethyltinlithium in tetrahydrofuran in the standard way.[51]

All the mixtures of 7 and 8 were unambiguously characterized by ^{13}C NMR spectroscopy[25] and mass spectroscopy (M^+). Elemental analyses were not obtained.

General Methods. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer while mass spectra were obtained on an AEI MS30 spectrometer using an ionizing energy of 70 eV. Vapor-phase chromatographic analyses were performed on a Varian 1740 gas chromatograph using a 10-ft column of 5% SE-30 on 100/120 Chromosorb W. All melting and boiling points are uncorrected. Liquid samples were purified by distillation in a Kugelrohr apparatus (Buchi GKR-50). Hence, the boiling points quoted pertain to the glass-oven temperature of the latter equipment.

NMR Spectra. The broad-band proton-decoupled ^{13}C NMR spectra were recorded in the pulse Fourier transform mode on a JEOL FX-90Q spectrometer operating at 22.53 MHz. The probe temperature was 295 ± 2 K. The spectral data listed in Table II were recorded on $CDCl_3$ solutions (*c* 0.2 M) in 10-mm tubes with Me_4Si as an internal reference (spectral width 4000 Hz, 16K/8K data points, minimum digital resolution of 0.02 ppm). Those listed in Table III were measured on c-C_6H_{12} solutions (*c* 0.2 M) in 10-mm tubes with benzene (7 μL) as an internal reference (spectral width 2000 Hz, 16K/8K data points, minimum digital resolution of 0.01 ppm). The ^{13}C NMR spectra[25] of the mixtures (7 and 8) were recorded in $CDCl_3$ and c-C_6H_{12} solutions (0.5 M) in a similar fashion.

The ^{19}F NMR spectra listed in Table IV of systems 7 and 8 were obtained under proton-decoupled conditions in the pulse Fourier transform mode with a JEOL FX-90Q spectrometer operating at 84.26 MHz. A spectral width of 2000 Hz was used, and the data were collected into 8K/4K data points, giving a resolution of better than 0.01 ppm. Each sample consisted of a mixture of the unsubstituted compounds (7 and 8, X = H; 3–4 mg) and substituted compounds (7 and 8, X; 4–5 mg) dissolved in 0.5 mL of the appropriate solvent.

^1H NMR spectra were measured with a Varian A60 spectrometer.

Registry No. 6 (X = NO_2), 80126-94-9; 6 (X = CN), 80126-95-0; 6 (X = COOH), 80126-96-1; 6 (X = $CONH_2$), 80126-97-2; 6 (X = $COOCH_3$), 80126-98-3; 6 (X = F), 74308-36-4; 6 (X = Cl), 80126-99-4; 6 (X = Br), 80127-00-0; 6 (X = I), 76807-82-4; 6 (X = NH_2), 80127-01-1; 6 (X = OH), 79963-10-3; 6 (X = OCH_3), 79963-08-9; 6 (X = CH_3), 67060-31-5; 6 (X = $Sn(CH_3)_3$), 76807-73-3; 6 (X = NH_3^+), 80127-02-2; 7 (X = NO_2), 80127-03-3; 7 (X = CN), 80127-04-4; 7 (X = COOH), 80127-05-5; 7 (X = $CONH_2$), 80127-06-6; 7 (X = $COOCH_3$), 80127-07-7; 7 (X = F), 72242-21-8; 7 (X = I), 76807-83-5; 7 (X = NH_2), 80127-08-8; 7 (X = OH), 80127-09-9; 7 (X = OCH_3), 80127-10-2; 7 (X = CH_3), 80127-11-3; 7 (X = $Sn(CH_3)_3$), 76807-75-5; 8 (X = NO_2), 80127-12-4; 8 (X = CN), 80127-13-5; 8 (X = COOH), 80127-14-6; 8 (X = $CONH_2$), 80127-15-7; 8 (X = $COOCH_3$), 80127-16-8; 8 (X = F), 72046-34-5; 8 (X = I), 76807-84-6; 8 (X = NH_2), 80127-17-9; 8 (X = OH), 80127-18-0; 8 (X = OCH_3), 80127-19-1; 8 (X = $Sn(CH_3)_3$), 76807-77-7.

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