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Proton Affinities of Substituted Benzaldehydes, 2-Phenylpropenes (α-Methylstyrenes), and Related Molecules: Calculational Studies and Comparison with Experimental Data

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Ab initio molecular orbital calculations, employing the STO-3G basis set, have been used to calculate proton affinities of substituted benzaldehydes and 2-phenylpropenes (α-methylstyrenes). The results are correlated with (an updated compendium of) Brown–Okamoto σ^+ values as well as with the Taft dual-substituent-parameter (DSP) equation. Comparisons are made with correlations of experimental gas-phase data. Comparisons of correlations of calculational and experimental data are made for benzenium and benzyl cations.

The structures of $C_7H_7^+$ ions and their derivatives have been a source of lively controversy over the past 20 years.[2] In some cases benzyl cations appear to be more stable, while tropylium ions are dominant in others.[3] An experimental study,[4] published over 20 years ago, of the ionization potentials of benzyl radicals gave a good correlation with Brown and Okamoto σ^+ values[5] and was though to implicate the intermediacy of benzyl cations. Correlation of the 11 IP values for monocyclic compounds disclosed in that study,[4] using Brown and Okamoto values[5] for σ^+, yields a slope (m) = −26.89, intercept (b) = −0.32, and correlation coefficient (r) = −0.987. Correlation with an updated compendium[6,7] of σ^+ gives m = −25.91, b = −0.14, and r = −0.987. The one data point that significantly deviates from this correlation corresponds to the p-cyano derivative [experimental ΔIP (relative to H) = −13.8 ± 2 kcal/mol; calculated $\Delta\Delta E$ (Brown and Okamoto[5] σ^+) = −18.0 kcal/mol; calculated $\Delta\Delta E$ (Exner[6] σ^+) = −18.3 kcal/mol]. The reason could lie in the fact that this derivative has the only π-withdrawing para substituent in the experimental gas-phase study, and accompanying destabilization of this benzyl cation could render cyanotropylium more stable. Howver, the fact that the Hückel charge densities for a tropylium and a p-benzyl cation position are both $+^1/_7$ indicates that there is no obvious reason for cyano being less destabilizing on a tropylium cation. Elimination of the p-cyano data point significantly improves the correlation. Thus, correlation (n = 10) with Brown and Okamoto σ^+ values yields m = −28.50, b = −0.71, and r = −0.995, and this corresponds to ρ = −19.6. Correlation with Exner's compendium of σ^+ values yields m = −27.58, b = −0.54, and r = −0.995, corresponding to ρ = −19.2.

Recently, Hehre et al.[8] published calculated (STO-3G) stabilization energies for benzyl cations. A plot of these data (n = 17) vs. Exner's σ^+ data provides m = −19.72, b = 0.56, and r = −0.983; the calculated slope is roughly 0.76 of the slope obtained by employing Lossing's experimental data.[4] MINDO/3[9] calculational data are also published for benzyl cations.[10] A good correlation is apparent upon exclusion of m- and p-cyanobenzyl cations. The remaining data (n = 10) yield n = −18.56, b = −0.82, and r = −0.984 by using the Exner σ^+ data.

The present study employs comparable minimal basis set ab initio molecular orbital calculations to obtain proton affinities of substituted benzaldehydes and 2-phenylpropenes (α-methylstyrenes). This work is relevant to the benzyl-tropylium cation controversy. Experimental gas-phase protonation energies have been obtained for derivatives of benzaldehyde and 2-phenylpropene.[11] Comparisons of calculated[12] and experimental[13] data indicate that the carbonyl group is the protonation site in benzaldehyde (and presumably those derivatives with cation-destabilizing ring substituents). The conclusion of Dewar and Landman[3] that O-protonated benzaldehyde (α-hydroxybenzyl cation) is more stable than O-protonated tropone (hydroxytropylium cation) rests upon their argument that MINDO/3 significantly overestimates stabilization in the tropylium cation. This is supported by the comparison of the respective MINDO/3[14] and experimental[15] values of $\Delta H_f°$(g) for benzaldehyde (−4.0 and −8.8 kcal/mol) and tropone (0.9 and 10.5 kcal/mol). That is to say, while MINDO/3 predicts that tropone is 4.9 kcal/mol less stable than benzaldehyde, experimental heats of formation indicate that it is 19.3 kcal/mol less stable

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Table I. Calculated (STO-3G) Total Energies of Substituted Tropylium Cations

substituent	total E, hartrees	ΔE_{stab},[a] kcal mol^{-1}	ΔE_{rel}, kcal mol^{-1}	
			m-benzyl	p-benzyl
H	−265.667 71	0	−9.66	−9.66
CH_3	−304.254 31	1.93	−9.66	−4.99
F	−363.124 395	−1.48	−14.41	−4.18
CF_3	−596.618 311	−8.87	−7.43	−8.70
CN	−356.196 376	−15.97	−6.29	−6.09
NH_2 (pyramidal)	−320.002 302			
NH_2 (planar conjugated)	−320.003 571	13.98	−21.50	2.56
NO_2 (planar conjugated)	−466.328 635	−20.95	−5.87	8.61
NO_2 (perpendicular)	−466.318 596			
OCH_3	−378.089 840	10.25	−21.32	−5.71

[a] Relative stabilization energies of tropylium ions (ΔE_{stab}, kcal mol^{-1}) are calculated according to eq 1. Energies relative to meta- and para-substituted benzyl cations (ΔE_{rel}) are also tabulated by using data from ref 8. (A negative ΔE_{rel} value means that the tropylium cation is more stable than the corresponding benzyl cation.)

Table II. Total STO-3G Energies (hartrees) of Substituted Benzaldehydes and Corresponding α-Hydroxybenzyl Cations

substituent (X)	benzaldehydes		α-hydroxybenzyl cations	
	meta	para	meta	para
H	−339.118 230	−339.118 230	−339.521 792	−339.521 792
F	−436.577 491	−436.578 213	−436.974 362	−436.981 938
CH_3	−377.701 369	−377.701 651	−378.106 988	−378.111 602
CH_3	−670.082 058	−670.082 068	−670.477 521	−670.476 203
CN	−429.668 553	−429.668 657	−430.057 854	−430.056 979
CH_3O	−451.531 790	−451.532 684	−451.934 514	−451.950 189
NH_2 (pyramidal)	−393.436 161	−393.437 543	−393.841 528	−393.859 715
NH_2 (planar)	−393.432 625	−393.434 243	−393.839 581	−393.860 557
NO_2 (planar)	−539.805 370	−539.805 499	−540.190 210	−540.186 547
NO_2 (perpendicular)	−539.797 454	−539.797 471	−540.181 323	−540.179 314

than benzaldehyde. Protonated 2-phenylpropene is intuitively reasonable as the α,α-dimethylbenzyl cation and this species is directly observable by NMR spectroscopy.[16] Thus, it is important to examine linear free-energy relationships for species in which substituted benzyl cations (e.g., protonated benzaldehydes and α-methylstyrenes) are accepted as the gas-phase ions and to compare the findings with those of the Lossing study[4] in which structural assignments are more ambiguous.

Methodology

The Gaussian 70 program series[17] and the STO-3G basis set[18] have been employed throughout the present investigation. Standard geometries[19] have been used for benzaldehydes, α-methyl styrenes, α-hydroxybenzyl cations, and α,α-dimethylbenzyl cations. Geometries of tropylium cations are based upon the published calculational structure of the parent ion.[20] A standard set of substituent geometries[21] has been utilized. Protonation energies are calculated through direct comparison of benzaldehydes and α-methylstyrenes with the corresponding protonated species, and relative protonation energies are obtained by setting the values for the parent hydrocarbons equal to

Table III. Calculated and Experimental Proton Affinities as Well as Relative Values for Substituted Benzaldehydes[a]

substituent (X)	calcd PA, kcal/mol	ΔPA(calcd), kcal/mol	exptl PA, kcal/mol	ΔPA(exptl), kcal/mol
H	253.1	0	198.2	0
m-F	248.9	−4.2	194.1	−4.1
p-F	253.2	0	196.7	−1.5
m-CH_3	254.4	1.3		
p-CH_3	257.1	4.0	201.8	3.6
m-CF_3	248.0	−5.1		
p-CF_3	247.2	−5.9	189.1	−9.1
m-CN	244.1	−8.9		
p-CN	243.5	−9.6	185.4	−12.8
m-CH_3O	252.6	−0.5		
p-CH_3O	261.8	8.8	210.8	12.6
m-NH_2	254.2	1.1		
p-NH_2	265.3	12.2		
m-NO_2	241.3	−11.7		
p-NO_2	239.0	−14.1		
p-Cl			197.6	−0.6

[a] Experimental values are ±2 kcal/mol and are obtained from ref 11.

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(19) A standard benzene ring geometry was employed throughout this study: C–C, 1.395 Å; C–H, 1.08 Å; benzylic C–C, 1.368 Å (see ref 20); for α-methyl groups, C–C, 1.50 Å, C–H, 1.09 Å, tetrahedral CH_3. For α-methylstyrene, coplanarity of the exocyclic group with the ring and 120° angles were assumed. The C_1–C_α bond length was 1.47 Å; C=C = 1.35 Å; C–CH_3 = 1.50 Å; for tetrahedral CH_3, all C–H = 1.10 Å. Benzaldehyde was assumed to be planar: C–CHO, 1.50 Å, C=O, 1.24 Å, C–H, 1.10 Å, all angles 120°. For protonated benzaldehyde: C–C_α, 1.368 Å; C–O, 1.271 Å; O–H, 1.003 Å; C–H, 1.114 Å; COH, 114.7°; other angles 120° and HCO bisected by plane of symmetry (based on calculated geometry of CH_2OH^+: Whiteside, R. A.; Binkley, J. S.; Krishnan, R.; DeFrees, D. J.; Schlegel, H. B.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive"; Carnegie-Mellon University, Pittsburg, PA, 1980. In all cases, the protonated benzaldehyde is calculated in the syn conformation.

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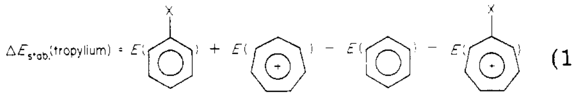
(21) Derivative substituents replace appropriate hydrogen: C–F, 1.35 Å. CH_3: C–C, 1.51 Å; C–H, 1.10 Å (tetrahedral). CF_3: C–C, 1.51 Å; C–F, 1.37 Å (tetrahedral). NO_2 (planar or perpendicular): C–N, 1.48 Å; N–O, 1.21 Å; angles, 120°. NH_2 (planar conjugated or planar perpendicular): C–N, 1.402 Å; N–H, 1.001 Å; angles, 120°; NH_2 (pyramidal): C–N, 1.402 Å; N–H, 1.001 Å; HNH, 113.1°; angle between HNH plane and ring plane, 37.5°. CN: C–C, 1.419 Å, C–N, 1.158 Å (linear). CH_3O: C–O, 1.36 Å, O–C, 1.43 Å, C–H, 1.09 Å; COC, 121° (tetrahedral CH_3). In both the protonated and unprotonated benzaldehydes as well as the α-methylstyrenes, meta substituents were chosen "cis" to the double bond.

Table IV. Total (STO-3G) Energies (hartrees) of Substituted α-Methylstyrenes and the Corresponding α,α-Dimethylbenzyl Cations

substituent (X)	α-methylstyrenes meta	α-methylstyrenes para	α,α-dimethylbenzyl cations meta	α,α-dimethylbenzyl cations para
H	−342.406 239	−342.406 239	−342.829 431	−342.829 431
F	−439.866 349	−439.866 183	−440.281 711	−440.290 323
CH_3	−380.989 242	−380.989 226	−381.414 557	−381.420 008
CN	−432.958 049	−432.958 621	−433.365 121	−433.364 142
CH_3O	−454.819 743	−454.819 647	−455.241 714	−455.260 037
NH_2 (pyramidal)	−396.724 140	−396.724 136	−397.148 853	−397.170 024
NH_2 (planar conjugated)	−396.720 461	−396.720 501	−397.146 892	−397.171 315
NO_2 (planar)	−543.095 680	−543.096 091	−543.497 662	[a]
NO_2 (perpendicular)	−543.087 571	−543.087 752	−543.488 471	−543.486 005

[a] Did not converge; therefore, p-NO_2 derivative was not part of the correlation analysis.

zero. Tropylium ion stabilization energies (ΔE_{stab}) are calculated according to isodesmic[22] eq 1. This approach



(1)

tends to cancel errors due to basis set deficiencies and lack of explicit electron correlation. A positive value for ΔE_{stab}(tropylium) corresponds to stabilization while a negative value connotes destabilization.

Although the results calculated are of the $\Delta\Delta E$ type (roughly equivalent to $\Delta\Delta H$ results), they are relevant to Hammett-type relationships which are linear free-energy relationships ($\Delta\Delta G$). One would anticipate that for a given reaction series, gas-phase entropy changes should remain essentially constant and that $\Delta\Delta S$ will be about zero. In fact, in their study of gas-phase basicities of substituted benzenes, Lau and Kebarle[13] showed that ΔS for protonation of both fluorobenzene and chlorobenzene was −3.5 ± 0.1 eu, in excellent agreement with the entropy change expected solely from the change in rotational symmetry number ($\Delta S_{rot} = -R \ln (12/2) = -3.56$ eu), and this assumption was employed in their analyses of the protonations of other substituted benzenes.

Results

In order to understand the experimental results, it is desirable to have energetics data for the isomeric substituted benzyl and tropylium cations. These data are summarized in Table I.

Calculated total energies of meta- and para-substituted benzaldehydes and the corresponding O-protonated cations are found in Table II. Pyramidal and planar amino derivatives and planar (conjugated) and perpendicular nitro derivatives have been investigated for this series as well as for the substituted tropyliums noted above. While p-nitrobenzyl cation is predicted to have a nitro substituent perpendicular to the ring,[10,23] this substituent is calculated to be planar in the para derivative of the α-hydroxybenzyl cation. In both cations the p-amino group is predicted to be planar rather than pyramidal. In Table III, calculated and experimental proton affinities as well as relative values are presented. While all of the calculated values are 51–58 kcal/mol too high, the agreement between experimental and theoretical relative proton affinities is good.[24]

Table V. Calculated and Experimental Proton Affinities as Well as Relative Values for Substituted α-Methylstyrenes[a]

substituent (X)	calcd PA, kcal/mol	ΔPA(calcd), kcal/mol	exptl PA, kcal/mol	ΔPA(exptl), kcal/mol
H	265.4	0	205.2	0
m-F	260.5	−4.9		
p-F	266.0	0.6	204.7	−0.5
m-CH_3	266.7	1.3		
p-CH_3	270.1	4.8	208.6	3.4
m-CN	255.3	−10.1		
p-CN	254.3	−11.1		
m-CH_3O	264.6	−0.8		
p-CH_3O	276.2	10.8	214.6	9.4
m-NH_2	266.3	1.0		
p-NH_2	280.4	15.1		
m-NO_2	252.1	−13.3		
p-Cl			203.0	−2.2
p-CF_3			197.1	−8.1

[a] Experimental values are ±2 kcal/mol and obtained from ref 11.

Calculated total energies of meta- and para-substituted α-methylstyrenes and the corresponding α,α-dimethylbenzyl cations are listed in Table IV. Again, the p-amino group in the cation is predicted to be planar. Since the calculation for the p-nitrobenzyl cation failed to converge, no decision could be made on the conformational preference of this group. Trifluoromethyl derivatives were not calculated due to a program limitation in the number of orbitals. In Table V calculated and experimental as well as relative values for the proton affinities of α-methylstyrenes are given. As in the case of the benzaldehydes, all of the calculated values are too high (by 60–64 kcal/mol). The experimental trends within the α-methylstyrene series also appear to be well reproduced. Although the calculations correctly predict that the proton affinities of α-methylstyrenes are generally higher than those of benzaldehydes, further analysis indicates some discrepancies. For example, the calculated proton affinity of p-methoxybenzaldehyde is 45 kcal/mol lower than that of α-methylstyrene, but the latter actually has the lower proton affinity. Thus, the intraset (e.g., benzaldehydes) comparison is better than interset comparison.[24]

Discussion

Table VI summarizes correlations of stabilization energies with σ^+ (Exner tabulation[6]), calculated with the STO-3G basis set, for derivatives of α-hydroxybenzyl, α,α-dimethylbenzyl, and tropylium cations examined in the present study. Additionally, calculational (STO-3G) studies performed by other researchers for benzyl and benzenium cations are included. Experimental gas-phase data are also correlated and listed in this table.

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[23] The (4-nitro-1-naphthyl)carbinyl cation also has this geometry: Greenberg, A.; Silverman, B. D., submitted for publication.

[24] This is a general phenomenon that arises from small and comparatively inflexible basis sets. The protonated and unprotonated species have the same number of electrons, but the former has more flexibility because of the additional basis functions of the hydrogen. As such, the unprotonated species is described poorer and has a comparatively higher total energy, and the resultant proton affinity is overestimated.

Table VI. Correlations of Stabilization Energies of Benzene-Derived Cations as Well as Tropylium Ions with σ^{+} [6]

cation	calcd				exptl			
	n	*m*	*b*	*r*	*n*	*m*	*b*	*r*
benzenium	21[a]	−21.83	0.37	−0.973				
	7[b]	−18.31	1.92	−0.979	8[c]	−18.39	1.69	−0.962
benzyl	17[d]	−19.72	0.56	−0.983	10[e]	−28.50	−0.71	−0.995
tropylium	8	−15.93	−3.48	−0.972				
α,α-dimethylbenzyl	12[f]	−14.04	−0.72	−0.987	6[g]	−13.28	−0.82	−0.997
α-hydroxybenzyl	15[h]	−12.18	−0.82	−0.976	8[i]	−15.87	−0.31	−0.980

[a] Employs all values reported in ref 12. [b] Calculated values[12] corresponding to seven of the eight para substituents employed in the experimental study.[13] [c] Employs values for only those ions corresponding to para protonation.[13] [d] Reference 8: these are isodesmic comparisons of benzyl cations. [e] Values from ref 4 with elimination of *p*-CN from the monocyclic data series. These data are said to correspond to ionization potentials of benzylic radicals. On the assumtion that benzylic C–H dissociation energies of substituted toluenes are nearly equal (see Table I; e.g., total energies of *m*- and *p*-methoxybenzyl radicals are almost equal), the stabilization energies are almost equivalent to isodesmic stabilization energies. [f] Obtained from calculated protonation energies of α-methylstyrenes (Tables V and VI). [g] From gas-phase protonation energies of α-methylstyrenes.[11] [h] Obtained from calculated protonation energies of benzaldehydes (Tables III and IV). [i] From gas-phase protonation energies of benzaldehydes.[11]

Table VII. Taft Correlations[36] of Calculational and Experimental Data

cation series	calcd							exptl						
	n	m_I	m_{R^+}	δ	*r*	rel ρ_{R^+}	λ[a]	*n*	m_I	m_{R^+}	δ	*r*	rel ρ_{R^+}	λ[a]
m-phenonium	8	−23.44	−2.49	0.44	0.970	0.136	0.106							
p-phenonium	8	−24.40	−19.19	1.60	0.985	1.046	0.786	6	−17.99	−18.28	1.70	0.987	0.607	1.016
m-benzyl	8	−21.15	−2.84	0.36	0.965	0.155	0.134	5	−28.00	−8.21	−0.45	0.994	0.293	0.293
p-benzyl	8	−20.78	−18.34	0.79	0.988	1.000	0.883	5	−32.11	−30.10	−0.86	0.997	1.000	0.937
tropylium	8	−21.83	−12.97	0.80	0.969	0.707	0.594							
m-α,α-dimethylbenzyl	7	−17.01	−2.91	−0.14	0.974	0.159	0.171							
p-α,α-dimethylbenzyl	6	−15.07	−11.56	0.50	0.981	0.630	0.767	6	−15.11	−13.28	−0.23	0.999	0.441	0.879
m-α-hydroxybenzyl	8	−14.73	−2.45	0.17	0.965	0.134	0.166							
p-α-hydroxybenzyl	8	−15.88	−9.87	0.61	0.977	0.538	0.622	7	−17.40	−16.71	−0.40	0.989	0.555	0.960

[a] $\lambda \equiv \rho_{R^+}/\rho_I$.

The most obvious feature of the calculational results is the decrease in slope as charge localization on the ring decreases (benzenium > benzyl > α,α-dimethylbenzyl > α-hydroxybenzyl). It is worth mentioning briefly that these slopes are *not* equivalent to ρ and that this latter quantity is obtained by using eq 2 if one assumes that $\Delta\Delta E° \simeq \Delta\Delta G°$.

$$\rho = (m\sigma^{+} + b)/2.303RT\sigma^{+} \qquad (2)$$

Although α,α-dimethylbenzyl and α-hydroxybenzyl cations have experimental slopes smaller than those of benzenium and benzyl cations as expected, their order is reversed. Furthermore, although the correlation of experimental benzyl stabilization values is excellent, the slope appears unreasonably high compared to the calculated value. More will be said about this problem later in the present paper. Finally, the relatively poor correlation for tropylium ions coupled with the fact that the intercept is 3.48 kcal/mol different from the expected value of 0.00 for the hydrogen "substituent" suggests that benzenoid σ^{+} values are not well suited to the tropylium ion.

A second approach for correlation analysis involves use of multiparameter treatments.[25] An example of this approach is the Taft dual-substituent-parameter (DSP) equation (eq 3).[26] "Universal" substituent parameters (σ,

$$\log k/k_0 = \sigma_I\rho_I + \sigma_R^{+}\rho_R^{+} + \gamma \qquad (3)$$

σ^{+}, etc.) are defined which should be independent of the ring system (benzyl, tropylium, etc.) and substitutional position. An instructive aspect of this approach is its ability to seemingly separate inductive and resonance effects. The factor λ ($=\rho_R^{+}/\rho_I$) is a measure of the relative importance of these effects at each substitutional site.[26] In the present investigation, eq 4 is employed for correlation of stabilization energies, and one may estimate ρ_I and ρ_R^{+} by dividing m_I and m_R^{+} by 2.303*RT*.

$$\Delta\Delta E = \sigma_I m_I + \sigma_R^{+} m_R^{+} + \delta \qquad (4)$$

Correlations of theoretical and experimental data by using the DSP approach are summarized in Table VII. The relative sensitivities to resonance effects (m_R^{+}) follow the expected trends. An interesting point is the difference in m_R^{+} values for tropylium vs. *p*-benzyl despite the fact that they have the same Hückel coefficients. To the extent that the LUMO coefficients reflect the charges at these two positions, the similarity of m_I values (Table VII) for tropylium and *p*-benzyl substituents is anticipated. However, the difference in conjugation effects between the para position of benzyl cation, an odd alternant hydrocarbon cation having a nonbonding LUMO, and a nonalternant aromatic cation such as tropylium, which has a strongly antibonding LUMO, has been discussed by Dewar and Landman.[3] The smaller value for m_R^{+} in tropylium relative to benzyl is consistent with their findings.

Once again the high sensitivities (m_I and m_R^{+}) for the experimental study by Lossing of the ionization potentials of benzylic radicals are well out of line with the experimental values on other cations. In particular, the high value of m_R^{+} for *m*-benzyl is hard to rationalize.

In order to gain another experimental handle on the validity of these calculations, we have calculated values of Δ*q* corresponding to the change in regional charge (carbon plus attached hydrogen[27]) upon conversion of ArH to $ArCH_2^{+}$[28] or of benzene to tropylium. Correlations of

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Table VIII. Listing of Comparable Values for Δq, m_{R^+}(calcd), m_{R^+}(exptl), and ^{13}C Chemical Shifts Useful for Correlations between These Quantities

molecule or ion	Δq[a]	m_{R^+}-(calcd)	m_{R^+}-(exptl)	^{13}C shift[e]
benzene	0			128.5
m-α-hydroxybenzyl cation	0.0525	−2.45		131.8
m-α,α-dimethylbenzyl cation	0.0539	−2.91		133.3
m-benzenium cation	0.0559	−2.49		139[b]
m-benzyl cation	0.0638	−2.84	−8.21	134.3[c]
p-α-hydroxybenzyl cation	0.1298	−9.87	−16.71	148.9
tropylium cation	0.1429	−12.97		155.4[d]
p-α,α-dimethylbenzyl cation	0.1519	−11.56	−13.28	155.9
p-benzyl cation	0.1905	−18.34	−30.10	167.3[c]
p-benzenium cation	0.2439	−19.19	−18.28	181[b]

[a] Change in regional charge[26] on transforming ArH → $ArCH_2^+$, $ArC(CH_3)_2^+$, etc. or benzene to tropylium. [b] Values obtained from: Olah, G. A.; Schlosberg, R. H.; Porter, R. D.; Mo, Y. K.; Kelly, D. P.; Mateescu, G. D. *J. Am. Chem. Soc.* 1972, *94*, 2034–2043. The values are subtracted from an assumed chemical shift of $^{13}CS_2$ (relative to Me_4Si) of 193.7 ppm. [c] Estimated by assuming equal chemical shift increments relative to α,α-dimethylbenzyl and α-methylbenzyl cations (see ref 28): i.e., $ArC(CH_3)_2^+ - ArCH^+CH_3 = ArCH^+CH_3 - ArCH_2^+$. [d] Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 91. [e] In parts per million from Me_4Si.

ρ_R^+ with experimental parameters such as ^{13}C response slope have been investigated by Forsyth and Sandel.[30] In Table VIII values of Δq are tabulated along with m_R^+ (calculated) and ^{13}C chemical shifts of relevant substituent-bearing carbons in the cation. Due to the inaccessibility of benzyl cation itself, chemical shifts for the meta and para carbons were estimated by using α-methylbenzyl and α,α-dimethylbenzyl cations as models.

The correlation of ^{13}C chemical shift (in parts per million from Me_4Si) with Δq is good: $n = 10$, $m = 226.0$, $b = 123.0$, $r = 0.984$. Correlation of m_r^+ with Δq is about comparable: $n = 9$, $m = -97.2$, $b = 2.54$, $r = -0.982$. The benzyl cation is calculated to behave quite normally.[31]

Conclusion

Calculations of proton affinities of benzaldehydes and α-methylstyrenes reproduce the trends and correlations of experimental gas-phase data. For example, both experimental and theoretical ρ^+ values are lower for these two classes of compounds than the proton affinities of substituted benzenes. This is expected on the basis of some charge localization on the α-carbon. There is a reversal of the two theoretical ρ^+ values for protonation of benzaldehydes and α-methylstyrenes relative to the experimentally derived values. Since the ρ^+ values correlate well with the change in regional charge (Δq) which in turn correlates with experimental ^{13}C chemical shift data, the discrepancy may be a result of experimental uncertainties in proton affinities.

The published correlation by Lossing[4] of ionization potentials of benzyl radicals with σ^+ yields a slope which appears too high. In particular, it is greater than the slope for protonation of substituted benzenes in contrast to intuitive and theoretical expectations. The same conclusions are obtained through an analysis using the Taft dual-substituent-parameter (DSP) equation. The inductive sensitivity (m_I, related to ρ_I) is anomalously high. Analysis of the calculated stabilization energies of substituted tropylium ions via the DSP equation indicates sensitivities to inductive effects comparable to benzyl cations but considerably lower sensitivity to conjugative effects. This is understandable in terms of the LUMO energies of benzyl and tropylium cations as previously discussed by Dewar and Landman.[10] In any case, interpretation of Lossing's experimental data is not readily apparent in terms of substituted benzyl cations.

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Registry No. Tropylium, 3551-27-7; Methyltropylium, 28454-59-3; fluorotropylium, 28454-58-2; (trifluoromethyl)tropylium, 81293-77-8; cyanotropylium, 45700-15-0; aminotropylium, 81293-78-9; Nitrotropylium, 64006-67-3; Methoxytropylium, 28454-61-7; α-hydroxybenzyl cation, 3441-73-4; *m*-fluoro-α-hydroxybenzyl cation, 81277-38-5; *p*-fluoro-α-hydroxybenzyl cation, 74597-36-7; *m*-methyl-α-hydroxybenzyl cation, 81277-39-6; *p*-methyl-α-hydroxybenzyl cation, 34256-03-6; *m*-(trifluoromethyl)-α-hydroxybenzyl cation, 81277-40-9; *p*-(trifluoromethyl)-α-hydroxybenzyl cation, 81277-41-0; *m*-cyano-α-hydroxybenzyl cation, 81277-42-1; *p*-cyano-α-hydroxybenzyl cation, 81277-43-2; *m*-methoxy-α-hydroxybenzyl cation, 81277-44-3; *p*-methoxy-α-hydroxybenzyl cation, 36323-61-2; *m*-amino-α-hydroxybenzyl cation, 81277-45-4; *p*-amino-α-hydroxybenzyl cation, 81277-46-5; *m*-nitro-α-hydroxybenzyl cation, 81277-47-6; *p*-nitro-α-hydroxybenzyl cation, 81277-48-7; benzaldehyde, 100-52-7; *m*-fluorobenzaldehyde, 456-48-4; *p*-fluorobenzaldehyde, 459-57-4; *m*-Methylbenzaldehyde, 620-23-5; *p*-methylbenzaldehyde, 104-87-0; *m*-(trifluoromethyl)benzaldehyde, 454-89-7; *p*-(trifluoromethyl)benzaldehyde, 455-19-6; *m*-cyanobenzaldehyde, 24964-64-5; *p*-cyanobenzaldehyde, 105-07-7; *m*-methoxybenzaldehyde, 591-31-1; *p*-methoxybenzaldehyde, 123-11-5; *m*-aminobenzaldehyde, 1709-44-0; *p*-aminobenzaldehyde, 556-18-3; *m*-nitrobenzaldehyde, 99-61-6; *p*-nitrobenzaldehyde, 555-16-8; α,α-dimethylbenzyl cation, 16804-70-9; *m*-fluoro-α,α-dimethylbenzyl cation, 25807-61-8; *p*-fluoro-α,α-dimethylbenzyl cation, 25807-60-7; *m*,α,α-trimethylbenzyl cation, 20605-65-6; *p*,α,α-trimethylbenzyl cation, 20605-66-7; *m*-cyano-α,α-dimethylbenzyl cation, 81277-49-8; *p*-cyano-α,α-dimethylbenzyl cation, 81277-50-1; *m*-methoxy-α,α-dimethylbenzyl cation, 77939-81-2; *p*-methoxy-α,α-dimethylbenzyl cation, 22666-71-3; *m*-amino-α,α-dimethylbenzyl cation, 81277-51-2; *p*-amino-α,α-dimethylbenzyl cation, 81277-52-3; *m*-nitro-α,α-dimethylbenzyl cation, 81277-53-4; *p*-nitro-α,α-dimethylbenzyl cation, 81277-54-5; α-methylstyrene, 98-83-9; *m*-fluoro-α-methylstyrene, 3825-81-8; *p*-fluoro-α-methylstyrene, 350-40-3; *m*,α-dimethylstyrene, 1124-20-5; *p*,α-dimethylstyrene, 1195-32-0; *m*-cyano-α-methylstyrene, 53097-35-1; *p*-cyano-α-methylstyrene, 19956-03-7; *m*-methoxy-α-methylstyrene, 25108-57-0; *p*-methoxy-α-methylstyrene, 1712-69-2; *m*-amino-α-methylstyrene, 23809-98-5; *p*-amino-α-methylstyrene, 1962-08-9; *m*-nitro-α-methylstyrene, 64416-49-5; *p*-nitro-α-methylstyrene, 1830-68-8.

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(31) Among the "reasonable" regularities is the finding that Δq for the meta carbons of all of the cations investigated here is much smaller than for the para carbons. Simple Hückel molecular orbital and valence bond theories both predict Δq for the meta carbons to be strictly 0.