Soc., **99**, 377 (1977).
(7) (a) See J. A. Pople, *Int. J. Mass Spectrom. Ion Phys.*, **17**, 1 (1976); (b) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11** (1974).
(8) (a) G. Hvistendahl and D. H. Williams, *J. Am. Chem. Soc.*, **96**, 6753 (1974); (b) *ibid.*, **96**, 6755 (1974); (c) *J. Chem. Soc., Chem. Commun.*, 4 (1975).
(9) G. Hvistendahl and D. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 881 (1975).
(10) J. W. McIver and A. Komornicki, *J. Am. Chem. Soc.*, **94**, 2625 (1972).
(11) M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, **99**, 1685 (1977).
(12) Using programs written by P. K. Weiner and A. Komornicki.
(13) S. Olivella, to be published.
(14) M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Am. Chem. Soc.*, **90**, 1953 (1968).
(15) G. P. Ford, to be published.
(16) W. A. Latham, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 808 (1971).
(17) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).
(18) (a) For results and a discussion of theoretical calculations on ethane, see J. W. Rabalais and A. Katrib, *Mol. Phys.*, **27**, 923 (1974). (b) For a discussion on methane, see R. N. Dixon, *Mol. Phys.*, **20**, 113 (1971); R, Manne, *ibid.*, **24**, 935 (1972).
(19) J. Weber and A. D. McLean, *J. Am. Chem. Soc.*, **98**, 875 (1976).
(20) B. Zurawski, R. Ahlrichs, and W. Kutzelnigg, *Chem. Phys. Lett.*, **21**, 309 (1973).
(21) M. L. Vestal in "Fundamental Processes in Radiation Chemistry", P. Ausloos, Ed., Wiley-Interscience, New York, N.Y., 1968.
(22) J. W. McIver, *Acc. Chem. Res.*, **7**, 72 (1974).
(23) J. Vogt and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 6682 (1975).
(24) M. W. Chase, J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Syverud and L. C. Walker, *J. Phys. Chem. Ref. Data*, **3**, 311 (1974).
(25) S. Saebø, *Chem. Phys. Lett.*, **40**, 462 (1976).
(26) Using a program written by C. E. Doubleday.
(27) J. H. Beynon, A. E. Fontaine, and G. R. Lester, *Int. J. Mass. Spectrom. Ion Phys.*, **1**, 1 (1968).
(28) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899, 4907 (1977).
(29) See footnote *b* in Table I.
(30) We used the GAUSSIAN 70 program as modified by A. Komornicki and W. Thiel.
(31) F. Bernardi, I. G. Csizmadia, H. B. Schlegel, and S. Wolfe, *Can. J. Chem.*, **53**, 1144 (1975).
(32) J. C. Polanyi and J. L. Schreiber, "Physical Chemistry", Vol. 6A, "The Kinetics of Gas Reactions", Chapter 6, Academic Press, New York, N.Y., 1974.

Gaseous Ions. 5.[1] Calculated (MINDO/3) Properties of Monosubstituted Tropylium Ions and Benzyl Cations

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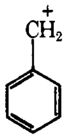
Abstract: Heats of formation, molecular geometries, and distributions of formal charge have been calculated by MINDO/3 for monosubstituted tropylium ions, and for monosubstituted benzyl cations with substituents in all possible positions (α, ortho, meta, para), for nine substituents (F, Cl, OH, NO_2, NH_2, CN, CH_3, ONO, OCH_3).

We recently reported[3] a MINDO/3[4] study of the conversion of benzyl cation (**1**) to tropylium (**2a**), a reaction which is believed to take place in the mass spectrometer. We concluded that it proceeds via two stable intermediates, the norcaradienium ion **3** and the cycloheptatrienium ion **4**. The calculated overall activation energy was quite high (32.7 kcal/mol), accounting for the failure to observe such rearrangements of benzyl cations in solution. We also studied the rearrangements of three derivatives (**5c–e**) of **1** to the corresponding tropylium ions (**2c–e**). The calculated properties of these ions were of interest from the point of view of the theory of substituent effects, the *p*-nitrobenzyl cation (**5e**) in particular having a nonplanar structure.

Recent experimental work[5] has suggested that derivatives of **1** may survive as such in the mass spectrometer under conditions where **1** itself is converted to **2**. The ions were obtained by loss of X from substituted toluene molecular ions of the type $(RC_6H_4CH_2X)^{+\cdot}$. Measurements of appearance potentials and wide range energy kinetics seemed to imply that when X = H, the resulting ions are benzylic if R = CH_3O, CH_3S, C_2H_5O, Cl, or Br, and tropenoid if R = CH_3, F, or OH; that when X = OPh the resulting ions are benzylic if R = CH_3O or NO_2 and tropenoid if R = CH_3, F, Cl, Br, or CF_3; and that when X = CH_3, the resulting ions are benzylic if R = NH_2 or CH_3O and tropenoid if R = OH, CH_3, F, Cl, Br, or CF_3. In the last case, however, comparisons of activation energies for loss of the methyl group from the precursor $(RC_6H_4C_2H_5)^{+\cdot}$ suggested that benzylic ions are also formed if R = F or CN and Lightner et al.[6] have claimed that benzylic ions are formed by loss of *n*-propyl from substituted *n*-butylbenzene molecular ions (i.e., X = *n*-Pr) if R = NH_2, CH_3O, HO, F, CH_3, CN, or NO_2.



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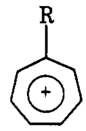
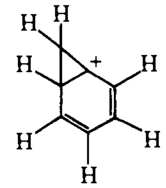


2a–k



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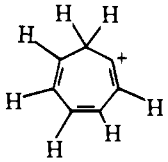

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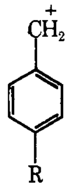
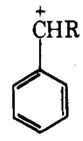
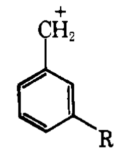


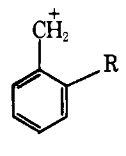
5b–k



6b–k



7b–k



8b–k

a, R = H; **b**, R = F; **c**, R = Cl; **d**, R = OH; **e**, R = NO_2; **f**, R = NH_2; **g**, R = CN; **h**, R = CH_3; **i**, R = ONO; **k**, R = OCH_3

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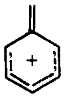

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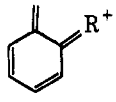

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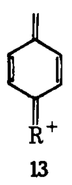

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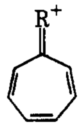

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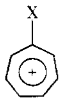
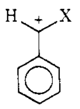
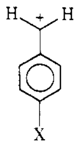
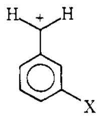
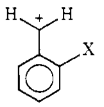
While these results seem to suggest that benzyl cation is stabilized relative to tropylium by $-E^7$ substituents such as NH_2 or OCH_3, there are several contradictory observations, for example, the claim that phenyl *p*-nitrobenzyl ether gave

Table I. Heats of Formation of Ortho, Meta, and Para Substituted Benzyl Ions and Tropylium Ions, Calculated by MINDO/3[a]

Substituent X					
H[b]	195.6 (209)	220.4 (216)	220.4	220.4	220.4
F	148.3	165.9	168.6	180.0	168.4
Cl[c]	191.2	208.2	212.2 (213)	281.4	214.0
OH[c]	133.7	146.7	149.3	166.6	150.9
NO_2[c]	200.4	217.7	215.1	217.0 (227)	216.8
NH_2	191.4	177.1	185.0	209.0	189.5
CN	219.6	235.1	240.8 (262)	243.0 (267)	243.9
CH_3	190.0	202.6	210.2 (202)	213.6 (206)	214.5
ONO[c]	162.5	170.2	175.3	196.0	178.4
OCH_3	145.0	148.5	159.8 (160)	175.5	158.1

[a] Experimental values (in parentheses) from J. L. Franklin, J. G. Dillard, N. M. Rosenstock, J. T. Nennon, K. Draxl, and F. M. Field, Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Ions", NSRDS-NBS 26, National Bureau of Standards, Washington, D.C., 1969. [b] See ref 3. [c] See ref 4.

rise to *p*-nitrobenzyl cation (**5e**) rather than nitrotropylium (**2e**). The relative effects of substituents also seem to vary irregularly. These discrepancies may be due in part to the difficulty of establishing the structures of ions formed in the mass spectrometer but there are also other possible complicating factors. For example, our calculations indicate the presence of a high barrier to the interconversion of **1** and **2a**. The product formed may then be determined kinetically, by the structure of the precursor, rather than by the relative stabilities of the two isomers. Indeed, our calculations indicated[8] that the interconversion of the toluene and cycloheptatriene molecular ions involves a transition state of lower energy than that for interconversion of **1** and **2a**. The balance between derivatives of **1** and **2a** could therefore be determined by a corresponding equilibrium between the precursors, i.e., the corresponding toluene and cycloheptatriene molecular ions.

The effects of substituents on the stabilities of **1** and **2a** are also of general interest in connection with theories of substituent effects, particularly in view of our preliminary results[1] concerning the effects of para substituents in **1**. We therefore decided to carry out a comprehensive study of the effects of a number of substituents in the various positions of **1** (α, ortho, meta, para), and in **2a**, on the properties of the two ions.

Procedure

The calculations were carried out by the standard MINDO/3[4] program.[9] All geometries were calculated by minimizing the energy with respect to all geometrical parameters, no assumptions of any kind being made. The minimizations were carried out using the standard[4,9] MINDO/3 version of the Davidon-Fletcher-Powell method.

Results and Discussion

Table I shows the heats of formation calculated for the monosubstituted tropylium ions (**2b-k**), and for monosubstituted benzyl cations with the substituent in any of the four possible positions (**5**, **6**, **7**, **8**; **b-k**), for nine different substituents, i.e., 47 ions including the two unsubstituted ones. In the few cases where experimental values are available for comparison they are listed in parentheses. The agreement is reasonably good except for tropylium (**2a**) and the cyanobenzyl cations (**5g**, **6g**). As we pointed out,[1,3] the discrepancy in the case of tropylium may be due, at least partly, to an unusually large difference between the vertical and adiabatic ionization potentials of the tropyl radical and to a consequent overestimation of the heat of formation of tropylium. In the case of the cyanobenzyl cations, the fault undoubtedly lies with MINDO/3 in view of its known[4] tendency to overestimate the stabilities of compounds containing CN groups.

The formal positive charge in **2a** is distributed uniformly round the ring, while that in **1**, according to simple MO theory, is concentrated at the active[10-12] positions, +4e/7 at the methylene group and +1/7 at each ortho or para position. On this basis one might expect electron-releasing substituents to stabilize **2a** and **1** to the same extent if they are attached at ortho or para positions in the latter, to stabilize **1** relative to **2a** if attached to the exocyclic (α) carbon, and to stabilize **2a** relative to **1** if attached to meta positions. The results in Table I show that such substituents (NH_2, OH, OCH_3) in the α position of **1** do indeed stabilize it relative to **2a**, but they also do so in the ortho and para positions. Indeed, in the case of NH_2, an exceptionally powerful −E substituent, substitution in *any* active position of **1** actually makes it more stable than aminotropylium. Clearly our naive argument, based essentially on a resonance-type argument, fails to account for the calculated substituent effects.

According to the PMO theory,[7,10,11] the large stabilizing effect of ±E and −E substituents in active positions of an odd AH (alternant hydrocarbon) cation arises from interactions between the filled bonding MOs of the substituent and the NBMO (nonbonding MO) of the ion. While this is a second-order perturbation, the MOs in question are unusually close together in energy so the effect is large (Figure 1a). In the case of an aromatic nonalternant cation, such as **2a** or cyclopropenium, the LUMO is no longer nonbonding, but antibonding, consisting indeed of a pair of degenerate antibonding MOs (Figure 1b). Interaction of these with a single −E substituent leaves one of them unchanged in energy,[12] while the interaction between the substituent and the other is smaller than in the case of an AH ion because the difference in energy between the interacting orbitals is greater. One would therefore expect ±E or −E substituents in the ortho-para positions of **1** to stabilize it more than they do **2a**, even though the formal charges at the relevant carbon atoms are the same in both cases.

The interaction between a substituent S and an even AH R can be shown[10-12] to be approximately the same for different AHs or different positions of attachment in a given AH. In the PMO treatment, the corresponding conjugation energy is absorbed into the bond energy of the RS bond; the conjugation energy between R and S consequently vanishing. A similar situation should exist in the case of aromatic nonalternant cations and indeed is exhibited very clearly by the effect of phenyl substituents in cyclopropylium (**9**). While phenyl groups at active positions are far more effective in stabilizing odd AH cations than are alkyl groups, the reverse is true in **9**. This is because[13] the conjugation energy in the latter case is

Table II. Comparison of the Effects of Substituents on the Heats of Formation of Tropylium and of Benzene

Substituent	Difference in heat of formation (kcal/mol) between $(RC_7H_6^+ - C_7H_7^+)$ calcd[a]	$(RC_6H_5 - C_6H_6)$ Calcd[a,b]	Obsd[b]
NH_2	−4.2	−10.9	+0.9
OH	−61.9	−57.3	−52.8
F	−47.3	−49.9	−46.3
Cl	−4.4	−7.7	−7.1
CH_3	−5.6	−5.3	−7.9
CN	+24.0	+20.1	+31.6

[a] Values calculated by MINDO/3. [b] Data from ref 5.

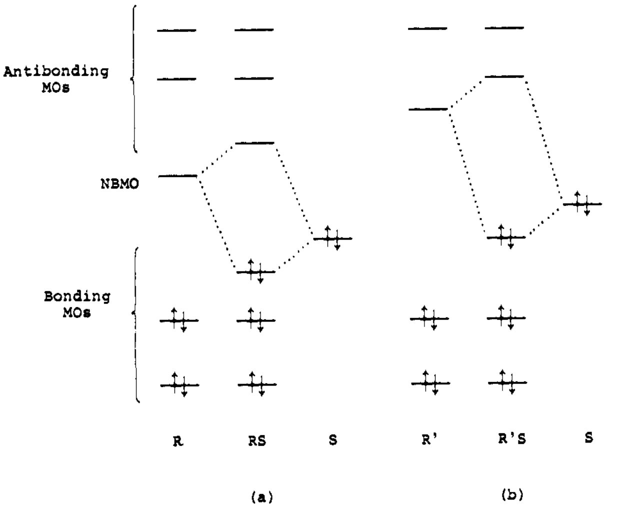


Figure 1. (a) Interaction between the filled AO of a simple −E substituent (S) and the NBMO of an odd AH cation (R) in RS; (b) analogous interaction in the case of a nonalternant odd cation R′.

effectively zero so stabilization arises from the −I effect of the substituent. The −I effect of alkyl is greater than that of phenyl.

A similar situation seems to hold in the case of tropylium. As Table II shows, the difference in heat of formation between tropylium and a monosubstituted tropylium is approximately the same as that between benzene and the corresponding monosubstituted benzene. The random differences in Table II can be attributed to the limited accuracy of MINDO/3. The substituents therefore seem to provide *no* conjugative stabilization of **2a**. This conclusion is supported by the data for the meta-substituted benzyl cations in Table I. Apart again from random scatter, the differences in energy between them and the corresponding monosubstituted tropylium ions are similar to that between **1** and **2a**.

For reasons previously indicated,[3] the difference in energy between **1** and **2a** is uncertain. Any error in the MINDO/3 value should, however, be duplicated in the case of derivatives so the MINDO/3 values for the effects of substituents on the difference should be reasonably reliable. According to our calculations, all our substituents stabilize **1** relative to **2a** and the most stable isomeric benzyl cation is that with the substituent in the α position, except for nitro, where the para isomer is the most stable. Assuming equilibrium, the stabilizing effects (kcal/mol) of the various substituents on **1** relative to **2a** are as follows:

$H < F < Cl < CN < NO_2$

(0) 7.2 7.8 9.3 10.1

$< OH < CH_3 < ONO < OCH_3 < NH_2$

11.8 12.2 17.1 21.3 39.1

This predicted order agrees quite well with the experimental findings. Note in particular the surprising difference between methoxyl, which very strongly stabilizes the benzyl cation, and hydroxyl, which is no more effective than the halogens or methyl. Note also the surprisingly strong stabilizing effect of nitro. This point will be discussed in detail later; here we will note only that our calculations are consistent with experiment on the assumption that equilibrium is attained, provided that the difference in energy between **1** and **2a** is ca. 10 kcal/mol, i.e., close to the experimental value. The MINDO/3 value for the heat of formation of **2a** would then be too negative by ca. 10 kcal/mol, an error not much greater than average and perhaps to be expected in view of the tendency[4] of MINDO/3 to underestimate angle strain.

Our calculations predict both *p*-aminobenzyl cation (**5f**) and *o*-aminobenzyl cation (**8f**) to be more stable than aminotropylium (**2f**), a conclusion in conflict with a recent report by Nibbering et al.[14] describing studies of benzylamine and *p*-toluidine by electron impact mass spectrometry. They claimed that the former gave an ion in which the benzyl skeleton was retained, presumably **6f**, whereas the latter gave **2f**. If the difference in energy between **1** and **2a** is indeed only ca. 10 kcal/mol, it is difficult to believe that **5f** would not lie below **2f** in energy. Further work on this problem is clearly needed.

Tables III–VII show the geometries calculated by MINDO/3 for the 47 cations.

As we have already noted,[3] the geometry calculated for **1** corresponds to a strong localization of bonds adjacent to the methylene group in the direction indicated by **10**. Thus the lengths of the C_1C_7 (1.37 Å) and C_1C_2 (1.47 Å) bonds are very similar to the lengths of the localized double (1.35 Å) and single (1.48 Å) bonds in classical polyenes[10] while those of the bonds in the pentadienate moiety (1.418, 1.385 Å) are similar to those calculated[15] by MINDO/3 for the all-cis-planar pentadienate cation **11** (1.421, 1.352 Å). This localization should tend to be reversed by −E substituents in the α position

Table III. Calculated Bond Lengths in α-Substituted Benzyl Cations (**6**)

Bond[a]	Bond lengths (Å) for substituent (R) H	F	Cl	OH	NO_2[b]	NH_2	CN	CH_3	ONO[c]	OCH_3[d]
C_1C_2, C_1C_6[e]	1.472	1.460	1.466	1.450	1.477	1.440	1.470	1.465	1.444	1.443
C_2C_3, C_5C_6[e]	1.385	1.391	1.390	1.397	1.382	1.400	1.390	1.391	1.399	1.395
C_3C_4, C_4C_5[e]	1.419	1.414	1.415	1.411	1.421	1.408	1.412	1.414	1.409	1.410
C_1C_7	1.370	1.384	1.387	1.424	1.381	1.452	1.395	1.402	1.437	1.439
C_7R	1.101	1.317	1.691	1.259	1.446	1.286	1.434	1.456	1.390	1.250

[a] For numbering see **1**. Ions coplanar except where noted. [b] The nitro group is orthogonal to the rest of the ring. NO bond length, 1.217 Å. [c] NO bond lengths: terminal, 1.164; central, 1.390 Å. [d] O–C (methyl) bond length, 1.368 Å. [e] In each case, the calculated lengths of the two bonds are the same to the third decimal place.

Table IV. Calculated Bond Lengths in Para-Substituted Benzyl Cations (**5**)

	Bond lengths (Å) for substituent (R)								
Bond[a]	F	Cl	OH	NO_2[b]	NH_2	CN	CH_3	ONO[c]	OCH_3[d]
C_1C_2, C_1C_6	1.479	1.475	1.483	1.469	1.484	1.472	1.472	1.485	1.484
C_2C_3, C_5C_6	1.375	1.381	1.368	1.390	1.363	1.381	1.379	1.367	1.365
C_3C_4, C_4C_5	1.419	1.427	1.456	1.432	1.467	1.440	1.440	1.458	1.462
C_1C_7	1.363	1.366	1.359	1.374	1.354	1.367	1.365	1.356	1.357
C_4R	1.333	1.720	1.277	1.374	1.303	1.453	1.484	1.268	1.250

[a] For numbering, see **1**. The ions are coplanar, except where noted. [b] The nitro group is orthogonal to the rest of the ion. NO bond length 1.219 Å. [c] NO bond lengths: terminal, 1.168; central, 1.369 Å. [d] O-C (methyl) bond length, 1.341 Å.

Table V. Calculated Bond Lengths in Meta-Substituted Benzyl Cations (**7**)

	Bond lengths (Å) for substituent (R)								
Bond[a]	F	Cl	OH	NO_2[b]	NH_2	CN	CH_3	ONO[c]	OCH_2[d]
C_1C_2, C_1C_6[e]	1.472	1.469	1.469	1.471	1.466	1.476	1.469	1.477	1.471
C_2C_3	1.380	1.385	1.406	1.407	1.410	1.401	1.404	1.405	1.402
C_3C_4	1.419	1.420	1.432	1.442	1.446	1.441	1.438	1.441	1.438
C_4C_5	1.413	1.417	1.410	1.416	1.405	1.417	1.417	1.390	1.411
C_5C_6	1.393	1.391	1.391	1.385	1.395	1.384	1.384	1.394	1.391
C_1C_7	1.374	1.372	1.373	1.373	1.373	1.369	1.370	1.369	1.372
C_3R	1.368	1.747	1.318	1.469	1.348	1.462	1.497	1.314	1.323

[a] For numbering, see **1**. All the ions are coplanar. [b] NO bond length, 1.216 Å. [c] NO bond lengths: terminal, 1.171; central, 1.343 Å. [d] O-C (methyl) bond length, 1.358 Å. [e] Bond lengths identical to three decimal places.

Table VI. Calculated Bond Lengths in Ortho-Substituted Benzyl Cations (**8**)

	Bond lengths (Å) for substituent (R)								
Bond[a]	F	Cl	OH	NO_2[b]	NH_2	CN	CH_3	ONO[c]	OCH_3[d]
C_1C_2, C_1C_6[e]	1.460	1.475	1.491	1.493	1.506	1.497	1.499	1.459	1.499
C_2C_3	1.398	1.399	1.436	1.400	1.465	1.410	1.410	1.447	1.443
C_3C_4	1.399	1.406	1.384	1.423	1.370	1.415	1.409	1.379	1.379
C_4C_5	1.439	1.427	1.444	1.407	1.453	1.416	1.420	1.450	1.446
C_5C_6	1.373	1.378	1.365	1.388	1.358	1.381	1.380	1.362	1.363
C_1C_7	1.365	1.368	1.362	1.373	1.356	1.369	1.369	1.358	1.360
C_2R	1.341	1.733	1.282	1.454	1.304	1.459	1.488	1.272	1.273

[a] For numbering, see **1**. The ions are coplanar, except where noted. [b] The nitro group is orthogonal to the rest of the ion. NO bond length, 1.218 Å. [c] NO bond lengths: terminal, 1.170; central, 1.373 Å. [d] O-C (methyl) bond length, 1.363 Å. [e] Bond lengths identical to third decimal place.

Table VII. Calculated Bond Lengths in Substituted Tropylium Ions (**2**)

	Bond lengths (Å) for substituent (R)									
Bond[a]	H	F	Cl	OH	NO_2[b]	NH_2[c]	CN	CH_3	ONO[d]	OCH_3[e]
C_1C_2, C_1C_7	1.405	1.407	1.411	1.437	1.424	1.430	1.425	1.431	1.434	1.443
C_2C_3, C_6C_7	1.405	1.392	1.398	1.382	1.411	1.397	1.401	1.402	1.426	1.381
C_3C_4, C_5C_6	1.405	1.424	1.414	1.430	1.396	1.413	1.409	1.410	1.377	1.427
C_4C_5	1.405	1.388	1.396	1.478	1.410	1.393	1.398	1.393	1.430	1.379
C_1R	1.108	1.352	1.741	1.292	1.492	1.376	1.466	1.501	1.294	1.280

[a] For numbering, see **2**. All the ions are coplanar, except where noted. [b] NO bond length, 1.217 Å. [c] The dihedral angles of the NH bonds relative to the ring are ±88.5°, the NH_2 group being pyramidal. [d] NO bond lengths: terminal, 1.168; central, 1.367 Å. [e] O-C (methyl) bond length, 1.348 Å.

of **1**, the resulting structures being isoconjugate with styrene, and the effect should increase with increasing −E activity of the substituent. This effect is evident in the results shown in Table III, the length of the C_1C_7 bond increasing, and that of the C_1C_2 or C_1C_6 bond decreasing, in the expected order, $F \sim Cl < OH \sim ONO \sim OCH_3 < NH_2$. In the case of NH_2, the C_1C_7 bond has indeed become longer than C_1C_2 or C_1C_6. It should be noted that the substituent does not destroy the C_2 symmetry of the ring in **1**, the calculated lengths of the C_1C_2 and C_1C_6 bonds agreeing in each case to the third decimal place, as also do those of the C_2C_3 and C_5C_6 bonds.

A −E substituent in an ortho or para position should on the other hand distort the geometry of **1** in the direction indicated by **12** or **13**, increasing the localization of the $C_1C_2C_6C_7$ bonds and introducing alternation into the pentadienate moiety. This effect is apparent in the results shown in Tables IV and VI and it again increases with increasing −E activity of the substituent. In the case of NH_2, the C_1C_2, C_1C_6, and C_1C_7 bonds have lengths characteristic of localized single and double bonds in classical polyenes while the remaining bonds on the ring alternate very strongly, e.g., 1.46, 1.37, 1.45, 1.36 Å in the case of the *o*-amino derivative.

Table VIII. Calculated Distribution of Formal Charge in α-Substituted Benzyl Cations (**6**)

	Formal charge (units of *e*) for substituent (R)									
Atom[a]	H	F	Cl	OH	NO_2	NH_2	CN	CH_3	ONO	OCH_3
C_1	−0.0908	−0.2143	−0.1489	−0.2095	−0.0321	−0.1166	−0.1051	−0.1189	−0.1924	−0.1733
C_2	0.1800	0.1636	0.1674	0.1417	0.1791	0.1019	0.1650	0.1631	0.1251	0.1205
C_3	−0.0730	−0.0476	−0.0576	−0.0350	−0.0703	−0.0158	−0.0630	−0.0617	−0.0314	−0.0290
C_4	0.2429	0.1981	0.2088	0.1590	0.2546	0.1186	0.2188	0.2095	0.1383	0.1419
C_5	−0.0730	−0.0589	−0.0576	−0.0350	−0.0626	−0.0158	−0.0630	−0.0617	−0.0343	−0.0349
C_6	0.1800	0.1816	0.1674	0.1417	0.1627	0.1019	0.1650	0.1631	0.1339	0.1370
C_7	0.2744	0.7346	0.4558	0.6260	0.0608	0.3116	0.3260	0.3282	0.6662	0.6382
R[b]	0.0476	−0.2405	0.0006	−0.3221	1.084[c]	0.0501	0.0073[d]	−0.0271	−0.5111[e]	−0.3176[f]

[a] For numbering, see **1**. [b] Formal charge for the atom in R adjacent to the methylene carbon. [c] Formal charge on each oxygen atom, −0.4804. [d] Formal charge on the nitrogen atom, 0.0951. [e] Formal charges on the nitrogen and terminal oxygen atoms: 0.7965, −0.2095, respectively. [f] Formal charge on the methyl carbon atom, 0.3630.

Table IX. Calculated Distribution of Formal Charge in Para-Substituted Benzyl Cations (**5**)

	Formal charge (units of *e*) for substituent (R)								
Atom[a]	F	Cl	OH	NO_2	NH_2	CN	CH_3	ONO	OCH_3
C_1	−0.1082	−0.0960	−0.0966	−0.0872	−0.0720	−0.0864	−0.0871	−0.0866	−0.0890
C_2	0.2001	0.1890	0.1900	0.1800	0.1630	0.1758	0.1792	0.1786	0.1800
C_3	−0.1907	−0.1295	−0.1908	−0.0342	−0.1408	−0.0886	−0.1005	−0.1931	−0.2000
C_4	0.6820	0.4200	0.6049	0.0597	0.3340	0.2841	0.2748	0.6247	0.6516
C_5	−0.1907	−0.1295	−0.1908	−0.0342	−0.1408	−0.0886	−0.1005	−0.1931	−0.2000
C_6	0.2001	0.1890	0.1900	0.1800	0.1630	0.1758	0.1792	0.1786	0.1800
C_7	0.2402	0.2503	0.2020	0.2945	0.1576	0.2565	0.2479	0.1791	0.1803
R[b]	−0.2560	−0.0429	−0.03620	1.0791[c]	−0.0081	0.0120[d]	−0.0116	−0.5365[e]	−0.4163[f]

[a] For numbering, see **1**. [b] Formal charge for the atom in R adjacent to the ring. [c] Formal charge at each oxygen atom, −0.4924. [d] Formal charge at the nitrogen atom, 0.0609. [e] Formal charges at the nitrogen and terminal oxygen atoms: 0.7969, −0.2472, respectively. [f] Formal charge at the methyl carbon atom, 0.4452.

Our arguments also imply that −E substituents at the meta position of **1** should have little effect on the geometry since the conjugation effects there correspond to those in a localized classical structure. The results in Table V show this to be the case. In the case of tropylium (Table VII), −E substituents do induce a moderate amount of bond alternation in the direction indicated by **14** but the changes are very much less than those induced by the same substituent in an ortho or para position of **1**. This confirms our previous conclusion, that conjugative effects of substituents in **2a** are small.

As one might also have expected, the changes in geometry brought about by the two +E substituents (CN, NO_2) are in all cases small. An interesting point here concerns the geometry of the nitro derivatives. The nitro group in *p*-nitrobenzyl cation had previously[9] been calculated to lie in a plane orthogonal to the benzene ring. We have now found that the same is true for the *o*- and α-nitro derivatives. This result is not surprising,[5] because the NO_2 group should[10,16] have a destabilizing mesomeric effect at any active position in an odd AH cation and an orthogonal orientation minimizes this unfavorable interaction. The situation should be quite different in the case of **2a**, where conjugation with substituents is much less important, and the nitro group in nitrotropylium was indeed calculated[5] to lie in the plane of the ring. Similar considerations should apply in the case of odd AH cations where the nitro group is attached to an inactive position and indeed we now find the *m*-nitrobenzyl cation (**7e**) to be planar, unlike the ortho and para isomers.

One surprising result is the prediction (Table VII) that the amino group in aminotropylium (**2f**) is orthogonal to the ring, unlike the hydroxy group in protonated tropone (**2d**) which is predicted to be planar. An experimental study of the geometry of the aminotropylium ion would be of interest. There seems no obvious reason why MINDO/3 should be in error in this particular case and if **2f** is indeed nonplanar, this would be a striking demonstration of the inefficient conjugation between −E substituent and the tropylium ring.

Tables VIII–XII show the distributions of formal charge calculated for the 47 ions.

The arguments given above indicate that the positive formal charges at all the active positions in **1** should decrease when a −E substituent is attached to any one of them, the ions being polarized in the sense indicated by **12**, **13**, or **14**. This effect is seen clearly (Tables VIII, IX, XI) for the active positions other than the one to which the substituent is attached. The charge of the latter, however, varies in an apparently erratic manner quite unrelated to the −E activity of the substituent. Thus in the case of the α-substituted ions **6**, the charges of the methylene carbon for various substituents R are

H, 0.27; F, 0.73; NH_2, 0.31; OCH_3, 0.64

Part of the difference can of course be attributed to polarity of the bond linking the substituent to carbon. This can be equated to the corresponding negative charge on the adjacent atom. These charges are, however, much smaller than the observed differences. Clearly some other factor must be operating.

The explanation probably lies in a basic difference between the conclusions of simple Hückel-type MO theories and those from more sophisticated SCF MO treatments. In the latter, a positive formal charge at a given atom Y increases the electronegativity of an adjacent atom X more than it does that of Y itself, while a negative formal charge has the opposite effect.[16] Thus in the case of C–F, where the intervening bond is polarized with F negative, $C^{\delta+}–F^{\delta-}$, the negative charge on fluorine decreases the electronegativity of carbon more than it does that of fluorine and the positive charge on carbon increases the electronegativity of fluorine more than it does that of carbon. The carbon atom is consequently *less* electronegative than it would be if the CF bond were nonpolar and it will

Table X. Calculated Distribution of Formal Charge in Meta-Substituted Benzyl Cations (**7**)

	Formal charge (units of *e*) for substituent (R)								
Atom[a]	F	Cl	OH	NO_2	NH_2	CN	CH_3	ONO	OCH_3
C_1	−0.0593	−0.0752	−0.0516	−0.1089	−0.0380	−0.0898	−0.0841	−0.0483	−0.0545
C_2	0.0189	0.1015	0.0178	0.2447	−0.0126	0.1582	0.1491	−0.0232	0.0127
C_3	0.3627	0.1301	0.3395	−0.2697	0.1699	−0.0166	−0.0254	0.3554	0.3268
C_4	0.1209	0.1819	0.0770	0.2845	0.1249	0.2268	0.2166	0.1061	0.1148
C_5	−0.0372	−0.0551	−0.0191	−0.0861	−0.0307	−0.0740	−0.0684	−0.0337	−0.0382
C_6	0.1583	0.1678	0.1361	0.2035	0.1453	0.1830	0.1729	0.1451	0.1505
C_7	0.2886	0.2829	0.2865	0.2916	0.2714	0.2760	0.2725	0.2695	0.2767
R[b]	−0.2409	−0.0602	−0.3985	1.1327[c]	−0.1471	0.0594[d]	0.0611	−0.5664	−0.4015

[a] For numbering, see **1**. [b] Formal charge at the atom in R adjacent to the ring. [c] Formal charge at each oxygen atom, −0.5180. [d] Formal charge at the nitrogen atom, 0.0035. [e] Formal charges at the nitrogen and terminal oxygen atoms, 0.8214, −0.2932, respectively. [f] Formal charge at the methyl carbon atom, 0.4090.

Table XI. Calculated Distribution of Formal Charge in Ortho-Substituted Benzyl Cations (**8**)

	Formal charge (units of *e*) for substituent (R)								
Atom[a]	F	Cl	OH	NO_2	NH_2	CN	CH_3	ONO	OCH_3
C_1	−0.1772	−0.1273	−0.1405	−0.0581	−0.0793	−0.0952	−0.1000	−0.1510	−0.1381
C_2	0.6520	0.3775	0.5858	−0.0105	0.3164	0.2215	0.2179	0.6100	0.5919
C_3	−0.2101	−0.1396	−0.2332	−0.0186	−0.1562	−0.0876	−0.1036	−0.2145	−0.2302
C_4	0.2537	0.2486	0.2429	0.2375	0.1908	0.2349	0.2413	0.2173	0.2303
C_5	−0.0869	−0.0766	−0.0771	−0.0620	−0.0445	−0.0679	−0.0712	−0.0684	−0.0732
C_6	0.1467	0.1596	0.1167	0.1945	0.0775	0.1668	0.1648	0.1018	0.1077
C_7	0.2840	0.2673	0.2381	0.2701	0.1439	0.2588	0.2507	0.2114	0.2713
R[b]	−0.2867	−0.0743	−0.3868	1.0769[c]	−0.0043	0.0112[d]	0.0007	−0.5462[e]	−0.3771[f]

[a] For numbering, see **1**. [b] Formal charge at the atom in R adjacent to the ring. [c] Formal charge at each oxygen atom, −0.5021. [d] Formal charge at the nitrogen atom, 0.0459. [e] Formal charges at the nitrogen and terminal oxygen atoms, 0.7935, −0.2466, respectively. [f] Formal charge at the methylic carbon atom, 0.3838.

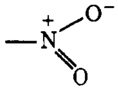
Table XII. Distribution of Formal Charge in Substituted Tropylium Ions (**2**)

	Formal charge (units of *e*) for substituent (R)									
Atom[a]	H	F	Cl	OH	NO_2	NH_2	CN	CH_3	ONO	OCH_3
C_1	0.0863	0.5711	0.2960	0.5422	−0.1411	0.3044	0.1454	0.1421	0.5886	0.5732
C_2	0.0863	−0.0830	0.0022	−0.1137	0.1510	−0.0095	0.0578	0.0423	−0.1109	−0.1176
C_3	0.0863	0.1423	0.1152	0.1523	0.0624	0.1125	0.0920	0.0988	0.1418	0.1465
C_4	0.0863	0.0559	0.0717	0.0437	0.1040	0.0705	0.0815	0.0779	0.0427	0.0436
C_5	0.0863	0.0559	0.0717	0.0437	0.1040	0.0705	0.0815	0.0779	0.0427	0.0436
C_6	0.0863	0.1423	0.1152	0.1523	0.0624	0.1125	0.0920	0.0988	0.1418	0.1465
C_7	0.0863	−0.0830	0.0022	−0.1137	0.1510	−0.0095	0.0578	0.0423	−0.1109	−0.1176
R[b]	0.0566	−0.2667	−0.0557	−0.3816	1.1040[c]	−0.2796	0.0289[d]	0.0175	−0.5896[e]	−0.4316[f]

[a] For numbering, see **2**. [b] Formal charge on the atom in R adjacent to the ring. [c] Formal charge on each oxygen atom, −0.5067. [d] Formal charge on the nitrogen atom, 0.0435. [e] Formal charges on the nitrogen and terminal oxygen atoms: 0.8169, −0.2573, respectively. [f] Formal charge on the methylic carbon atom, 0.4378.

be correspondingly ready to give up electrons to other adjacent atoms. This effect is responsible for the well-known alternation of charges calculated by SCF treatment[17] and it leads of course to unexpectedly large positive charges on carbon atoms adjacent to highly electronegative atoms.

This effect is of course diametrically opposite to that expected on the basis of simple MO theories where the positive charge on carbon adjacent to fluorine is expected to make it *more* electronegative, not less, a view which seems to be supported by current ideas concerning the π inductive effect.[18] The latter, however, refer to cases CX where the atom in X adjacent to carbon is *positively* charged, e.g.



, $—C^{\delta+}F_3^{\delta-}$

and where the electronegativity of the adjacent carbon atom is indeed increased. In the case of substituents such as F or OCH_3, the inverted π inductive effect will lead to electron release indistinguishable from that due to a genuine −E mesomeric effect by the substituent. Indeed, it seems very likely that the apparent −E effect of fluorine arises almost entirely from this source because it seems improbable that so electronegative an element could act as a π donor to carbon. According to this view, the π polarization in such cases arises neither from active sharing of p electrons of fluorine, nor from exchange repulsions between the low pair electrons of fluorine and filled π MOs, but from the reduction in electronegativity of the carbon atom adjacent to fluorine by the electrostatic effect of the adjacent negatively charged fluorine atom.

So far we have considered only the effects of substituents attached at the active positions in **1**. Substituents at the (inactive) meta position, or in the nonalternant tropylium ion (**2a**), are expected to have little effect on the distribution of formal charge in view of their anticipated lack of mesomeric interactions and the small changes they induce in the geometries of **1** and **2a**. Indeed, apart from the expected positive formal charges at carbon atoms adjacent to very electronegative atoms in the substituents (F, OR), the distributions of formal charge are very similar to those in **1** and **2a** (Tables X, XII).

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References and Notes

(1) Part 3: M. J. S. Dewar and D. Landman, *J. Am. Chem. Soc.*, submitted for publication.
(2) Robert A. Welch Postdoctoral Fellow.
(3) C. Cone, M. J. S. Dewar, and D. Landman, *J. Am. Chem. Soc.*, submitted for publication.
(4) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1294, 1302, 1307 (1975); M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *ibid.*, **97**, 1311 (1975).
(5) J. T. Bursey, M. M. Bursey, and D. G. I. Kingston, *Chem. Rev.*, **73**, 191 (1973).
(6) D. A. Lightner, S. Majeti, R. Nicoletti, and E. Thommen, *Intra-Sci. Chem. Rep.*, **6**, 113 (1972).
(7) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3350 (1952).
(8) M. J. S. Dewar and D. Landman, *J. Am. Chem. Soc.*, submitted for publication.
(9) Available from QCPE.
(10) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969.
(11) M. J. S. Dewar and R. C. Dougherty, "The PMO Theory of Organic Chemistry", Plenum Press, New York, N.Y., 1975.
(12) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3341 (1952).
(13) Reference 11, p 295.
(14) A. P. Bruins, N. M. M. Nibbering, and T. J. de Boer, *Tetrahedron Lett.*, 1109 (1972).
(15) Unpublished work by F. Carrion.
(16) M. J. S. Dewar and I. J. Turchi, *J. Am. Chem. Soc.*, submitted for publication.
(17) See, e.g., W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 2191 (1970).
(18) M. J. S. Dewar and A. P. Marchand, *J. Am. Chem. Soc.*, **88**, 3318 (1966); M. J. S. Dewar and Y. Takeuchi, *ibid.*, **69**, 390 (1967).

On a Recent Attempt to Apply Frontier Orbital Theory to Nucleophilic Aromatic Substitution

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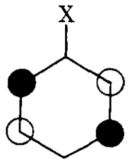
Abstract: The recent attempt by Epiotis and Cherry to apply frontier orbital formalism to nucleophilic aromatic substitution in polyhaloaromatics is criticized. It is shown that, contrary to the original claim, the method cannot be convincingly applied to substituted benzenes, and that it cannot give correct predictions in the cases of a number of perfluoropolycyclic aromatics for which experimental results are available. An extension of the older, "1_π-repulsion", method is presented which can rationalize the substitution reactions of these perfluoropolycyclics.

The recent publication[1] by Epiotis and Cherry of a frontier orbital (FO) method purporting to predict the orientation of nucleophilic substitution in polyfluorobenzenes and related species prompts us to reply. Their publication fails to give any convincingly coherent explanation of the experimental facts, and is, indeed, greatly inferior to one published[2] 10 years ago.

The essence of Epiotis and Cherry's FO approach is a consideration of the interaction between the LUMO of the benzenoid substrate and the HOMO of the incoming nucleophile. The latter orbital may be considered for practical purposes to be of at least cylindrical symmetry, and so attention focusses upon the LUMO of the substrate. Epiotis and Cherry analyze the problem of lifting the degeneracy of the two low-lying π-type benzenoid orbitals 1 and 2 in the presence of a substituent X and show that the FO hypothesis leads to the result that in C_6F_5X compounds where the substituent induced energy difference between 1 and 2 is large (i.e., X is a strong donor or strong acceptor of electrons), then either (1) substitution should be nearly all para to X (if 2 is lowest lying), or (2) equal amounts of substitution are expected meta and ortho to X (if 1 is). This latter prediction is obviously not in accord with experiment, and the authors seek to avoid the difficulty by invoking steric effects to disqualify ortho substitution.



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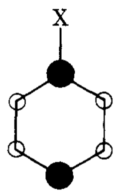

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Even so, however, the FO approach does not explain the known facts: the experimental result is that, for clear-cut cases with strong acceptors (e.g., $C_6F_5NO_2$)[3] or donors (e.g., $C_6F_5NH_2$)[4] either (1) ortho and para substitution is observed with essentially no meta or (2) meta substitution is very predominant with little or no ortho or para product found. (There are, naturally, intermediate cases, but these are not germane here.)

The attempt to cover case (2), where experiment gives essentially all meta product, by saying that the simple FO method predicts ortho + meta attack, but ortho is ruled out by steric effects, is very difficult to sustain. Thus, reaction of pentafluorophenoxide ion with hydroxide ion gives essentially only meta product,[5] whereas the steric effect of O^- vs. F must be at best minimal, as indeed must that for NH_2 vs. F in pentafluoroaniline,[4] where meta substitution is again almost the exclusive reaction. It may thus be fairly concluded that the attempt to distort the FO conclusion to fit the experimental results fails here.

It should be pointed out here that these experimental observations are all satisfactorily rationalized on the older[2] "I_π-repulsion" theory, based upon electron repulsions in anionic Wheland intermediates, no universal steric effect being needed.

Turning now from benzenes to perfluoropolycyclics, where