Ab Initio SCF Computations on Toluene and the Toluenium Ion Using a Large Contracted Gaussian Basis Set

Walter C. Ermler and Robert S. Mulliken*[1]

Contribution from the Department of Chemistry, University of Chicago, Chicago, Illinois 60637. Received August 18, 1977

Abstract: Improved SCF computations on the toluene molecule and on the toluenium ion (protonated toluene), using a large contracted Gaussian basis set including polarization functions, are reported. One-electron properties are tabulated and compared. A population analysis for σ, π (and quasi-π), and total overlap populations and atomic charges are reported and discussed. The nature of the weak (sacrificial) hyperconjugation in toluene and the stronger hyperconjugation in toluenium ion is discussed. The dipole moment of toluene is computed in agreement with experiment, although the population analysis indicates that the methyl group as a whole is somewhat negative.

This paper is a contribution to the detailed understanding of hyperconjugation (HCJ) in the p-toluenium ion, and also contains the most accurate SCF computation to date on toluene. A similar paper on the benzenium ion and benzene was recently published.[2] Our original intention was to do similar work on other methylated benzenium ions, but because of the large amount of computing time required, and our belief that p-toluenium (CH_3 group para to H_2 group) illustrates well the main features of methyl HCJ in arenium ions, we are not now contemplating additional work. Further, as Hehre et al. have shown, much can be deduced by simpler calculations in conjunction with experiment.[3]

For toluene, where such matters as the dipole moment and the electric field gradients at various atoms are of interest, Hehre et al. have earlier reported their results for a minimal-basis SCF computation.[4] Previously, only semiempirical results were available. Early π-electron-only Hückel-type calculations should also be mentioned.[5]

For toluenium, there are four possible isomers, with the methyl group attached para, ortho, or meta to the position of the extra proton or (ipso) at the same carbon as the latter. Minimal-basis STO-3G calculations[3] indicate that the para form is moderately more stable than the ortho and both are considerably more stable than the other two, whose proton affinities are near those of benzene. These relations can be understood by drawing HCJ resonance structures for p-toluenium as shown in Figure 1, with similar structures for o-toluenium. Both show proton HCJ as in benzenium *plus* quinoid HCJ. For m-toluenium, the quinoid structure is impossible, so that it has only proton HCJ. HCJ in *ipso*-toluenium is similar to that in benzenium.

We have chosen to restrict our computations to p-toluenium because (1) it is no doubt the predominant isomer, and (2) its relatively high symmetry facilitates the computations. Further,

we restrict ourselves to having two H atoms of the CH_3 group on a line parallel to the ring plane ("orthogonal arrangement" in the notation of Hehre et al.[4]). The symmetry is then C_s. It is reasonably clear that other orientations of CH_3 would not appreciably change the nature of our conclusions. Experimentally, a rotation barrier of 14 cal/mol is reported.[6]

The SCF computations for toluene and the toluenium ion were done using the (11s 7p 1d/7s 1p)/[5s 3p 1d/3s 1p] basis set of contracted Gaussian-type functions as reported in Table I of ref 2. The geometric parameters chosen for the calculations on toluene and toluenium are shown in Figure 2. Those for toluene correspond to the benzene skeleton with a replacement by a methyl group having tetrahedral HCH angles. Those for toluenium correspond to the optimum benzenium parameters (ref 2, Figure 2) with a methyl group substituted as in toluene. Thus, we assume that the $R(C_1C_{2,6})$ distances and the $H_1C_1H_7$ angle, which were optimized in the benzenium study, are unchanged in toluenium.

Results and Discussion

Energies. In Table I are given the computed energies of the various MOs. Because of the low symmetry, there are only two species of MOs, a' and a". However, for comparison with benzene and benzenium, symbols for the corresponding MOs of both the latter are given in parentheses. The correspondence is in general only approximate. Further, toluene and toluenium contain four more MOs than benzene and benzenium because of the presence of the CH_3 group instead of an H atom. The corresponding methyl group MOs are indicated in parentheses preceded by an M: Mla_1, $M2a_1$, Mle_x, Mle_y; Mle_x is the quasi-π group orbital of the CH_3 group.

Further, note that because in the region of the CH_3 group the ring plane is no longer rigorously a plane of symmetry, there is a small amount of mixing of σ with π and quasi-π or-

Table I. Energy Quantities (hartrees) for Toluene and the Toluenium Ion. Comparison with Benzene and Benzenium

Molecular orbital[a]	Benzene -230.7771^c	Toluene -269.8245^c	Toluenium -270.1399^c	Benzenium -231.0784^c
$1a'(1a_{1g}, 1a_1)$	-11.238	-11.240 (ϵ_1)	-11.496 (ϵ_1)	-11.495
$2a'(1e_{1u}, 2a_1)$	-11.238	-11.235 (ϵ_2)	-11.472 (ϵ_3)	-11.488
$1a''(1e_{1u}, 1b_2)$	-11.238	-11.235 (ϵ_3)	-11.472 (ϵ_2)	-11.488
$3a'(1e_{2g}, 3a_1)$	-11.236	-11.230 (ϵ_4)	-11.435 (ϵ_4)	-11.449
$2a''(1e_{2g}, 2b_2)$	-11.236	-11.230 (ϵ_5)	-11.428 (ϵ_5)	-11.437
$4a'(M1a_1)$		-11.230 (ϵ_6)	-11.428 $(\epsilon_6)^b$	-11.437
$5a'(1b_{1u}, 4a_1)$	-11.236	-11.229 (ϵ_7)	-11.404 $(\epsilon_7)^b$	
$6a'(2a_{1g}, 5a_1)$	-1.152	-1.154 (ϵ_8)	-1.369 (ϵ_8)	-1.375
$7a'(2e_{1u}, 6a_1)$	-1.016	-1.043 (ϵ_9)	-1.263 (ϵ_9)	-1.254
$3a''(2e_{1u}, 3b_2)$	-1.016	-1.013 (ϵ_{10})	-1.220 (ϵ_{10})	-1.230
$8a'(M2a_1)$		-0.928 (ϵ_{11})	-1.134 (ϵ_{11})	
$4a''(2e_{2g}, 4b_2)$	-0.825	-0.827 (ϵ_{12})	-1.034 (ϵ_{12})	-1.038
$9a'(2e_{2g}, 7a_1)$	-0.825	-0.795 (ϵ_{13})	-1.011 (ϵ_{13})	-1.062
$10a'(3a_{1g}, 8a_1)$	-0.710	-0.692 (ϵ_{14})	-0.893 (ϵ_{14})	-0.922
$5a''(M1e_y)$		-0.634 (ϵ_{15})	-0.843 (ϵ_{15})	
$11a'(2b_{1u}, 9a_1)$	-0.644	-0.631 (ϵ_{16})	-0.837 (ϵ_{16})	-0.863
$6a''(1b_{2u}, 5b_2)$	-0.621	-0.587 (ϵ_{17})	-0.785 (ϵ_{18})	-0.842
$12a'(1a_{2u}, 1b_1)*$	-0.501	-0.575 (ϵ_{18})	-0.801 (ϵ_{17})	-0.811
$13a'(3e_{1u}, 10a_1)$	-0.589	-0.563 (ϵ_{19})	-0.764 (ϵ_{19})	-0.800
$7a''(3e_{1u}, 6b_2)$	-0.589	-0.536 (ϵ_{20})	-0.713 (ϵ_{21})	-0.794
$8a''(3e_{2g}, 7b_2)$	-0.496	-0.490 (ϵ_{21})	-0.684 (ϵ_{23})	-0.699
$14a'(M1e_x)*$		-0.487 (ϵ_{22})	-0.745 (ϵ_{20})	
$15a'(3e_{2g}, 11a_1)$	-0.496	-0.484 (ϵ_{23})	-0.691 (ϵ_{22})	-0.715
$9a''(1e_{1g}, 1a_2)*$	-0.337	-0.335 (ϵ_{24})	-0.539 (ϵ_{25})	-0.546
$16a'(1e_{1g}, 2b_1)*$	-0.337	-0.323 (ϵ_{25})	-0.612 (ϵ_{24})	-0.640

[a] In parentheses are given the most nearly corresponding MOs of benzene (symmetry D_{6h}), of benzenium (symmetry C_{2v}), and of the CH_3 group (symmetry C_{3v}; indicated by M). The hyperconjugation MOs (π and quasi-π) are indicated by an asterisk. [b] In toluenium, a' has the form $(1b_{1u}, 4a_1)$ and 5a' the form $(M1a_1)$. [c] Total energy.
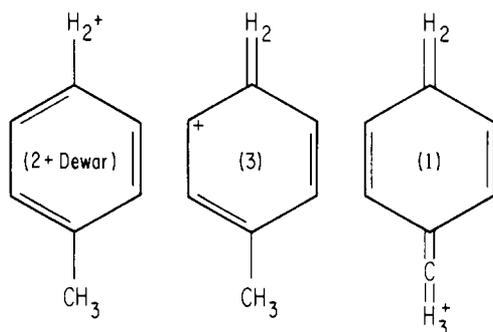
Figure 1. Resonance structures in *p*-toluenium. The number of similar structures is indicated in the middle of the ring.

Figure 2. Toluenium geometry. Distances $R(C_4C_{4M})$ and $R(C_{4M}H_{4M1,2,3})$ taken from F. A. Keidel and S. H. Bauer, *J. Chem. Phys.*, **25**, 1218 (1956).

bitals. This is a minor effect which appears in our computed tables of LCSTF coefficients, but it does not seem worthwhile to record the details here.

In Table I, the (slightly imperfect) π and quasi-π MOs are marked with an asterisk. Comparing toluenium with toluene in Table I, corresponding ϵ's are for obvious reasons all increased in the latter. The downward shifts are largest for the a' MOs of toluenium which are π or quasi-π MOs involved in HCJ. The a" π-type MO is not so involved. Its form (see Table VI) is very nearly the same in toluenium as in toluene, and also as in benzenium and benzene. This MO corresponds to one component of the $1e_{1g}$ MO of benzene.

Comparing toluene with benzene in Table I, there are additional MOs because of the substitution of a CH_3 group for an H atom. However, most of the remaining MOs are only moderately displaced in toluene as compared with corresponding MOs in benzene. Exceptions are the hyperconjugated MO 12a', which is considerably pushed down in toluene, and the 7a" MO, which is considerably pushed up. Comparing toluenium with benzenium in Table I, displacements are mostly moderate, but 9a', 6a", and 7a" are considerably pushed up.

Other Properties. The electric field gradients centered at the symmetry unique nuclei are listed in Table II. Together with the total electric field gradients are listed the nuclear (q^N) and electronic contributions due to the σ (q^σ) and π or quasi-π (q^π) MOs (see Table I).

The **q** centered at the hydrogen nuclei are seen to be relatively insensitive to the ring position, although the values at the methyl hydrogens are smaller (~ 0.03 au) than those at the ring hydrogens. This is the case in both toluene (T) and toluenium (TH^+) and is true in spite of some rather large, but compensating, changes in the σ and π contributions. This trend was also seen in benzene (B) and benzenium (BH^+) where the values in B were slightly reduced at the ortho and para positions.[2] These results support the suggestion that the protonation results in a rearrangement such that all the hydrogen atoms are roughly equivalent, as deduced from their electric field gradients, with methyl hydrogens being somewhat less positive than ring hydrogens.

Table II. Electric Field Gradients of Toluene (T) and Toluenium (TH$^+$)[a,b]

Center		q_{bb}	q_{bb}^N	q_{bb}^σ	q_{bb}^π	q_{cc}	q_{cc}^N	q_{cc}^σ	q_{cc}^π	ϕ,[c] deg
T	C$_1$	−0.215	0.676	−1.418	0.527	−0.130	0.314	−0.922	0.478	
TH$^+$		0.017	0.380	−1.105	0.741	−0.034	0.212	−0.897	0.651	
T	C$_2$	−0.245	0.695	−1.365	0.424	−0.149	0.300	−0.942	0.493	
TH$^+$		−0.412	0.619	−1.333	0.302	−0.352	0.342	−1.043	0.349	−21.0 (*YZ*)
T	C$_3$	−0.218	0.796	−1.444	0.428	−0.114	0.235	−0.887	0.538	2.6 (*YZ*)
TH$^+$		−0.103	0.791	−1.423	0.529	−0.154	0.238	−0.951	0.559	−6.5 (*YZ*)
T	C$_4$	−0.251	0.517	−1.273	0.505	−0.156	0.632	−1.179	0.392	
TH$^+$		−0.472	0.518	−1.290	0.300	−0.460	0.629	−1.313	0.225	
T	C$_{4M}$	−0.015	−0.207	−0.545	0.738	0.026	0.476	−0.939	0.490	14.7 (*XZ*)
TH$^+$		−0.098	−0.206	−0.621	0.731	0.150	0.531	−1.044	0.664	1.4 (*XZ*)
T	H$_1$	−0.143	−0.734	0.515	0.075	0.313	1.699	−1.281	−0.105	
TH$^+$		−0.134	−0.737	0.478	0.126	0.267	1.568	−1.056	0.225	−13.4 (*XZ*)
TH$^+$	H$_7$	−0.134	−0.737	0.479	0.125	0.287	1.568	−1.060	−0.221	−13.4 (*XZ*)
T	H$_2$	−0.145	−0.728	0.513	0.070	0.312	1.697	−1.285	−0.100	
TH$^+$		−0.145	−0.714	0.525	0.044	0.294	1.685	−1.312	−0.079	
T	H$_3$	−0.142	−0.640	0.443	0.055	0.313	1.648	−1.245	−0.091	
TH$^+$		−0.132	−0.639	0.425	0.082	0.300	1.648	−1.25^8	−0.090	
T	H$_{4M1}$	−0.134	−0.606	0.370	0.102	0.274	1.414	−0.884	−0.256	
TH$^+$		−0.126	−0.601	0.379	0.096	0.267	1.410	−0.898	1−0.245	
T	H$_{4M2}$	−0.130	−0.539	0.323	0.086	0.272	1.394	−0.985	−0.137	
TH$^+$		−0.122	−0.532	0.332	0.078	0.262	1.390	−0.985	−0.142	

[a] All values are in atomic units relative to the principal axis system. The bb and cc axes are (approximately) perpendicular to, in the plane of the ring, and parallel to the CH bond directions, respectively. The third component may be obtained from the traceless condition $q_{aa} = -(q_{bb} + q_{cc})$. [b] Eight misprints in Table V of ref 2 are noted here. The corrected values are listed as the (row, column) entry: (3, 5) = 2.444; (4, 3) = −0.647; (7, 3) = −1.290; (11, 3) = −1.080; (12, 3) = 0.335; (16, 4) = 0.770; (23, 2) = −1.043; (24, 2) = −0.234. [c] The deviations of the principal axis system from the respective C–H bond directions in the *YZ* or *XZ* planes (where the ring is in the *YZ* plane) are denoted in parentheses. Rotation angles less than 1° are not reported.

The carbon atoms are significantly charged as a result of protonation, again with marked similarities to the B and BH$^+$ results. To facilitate comparisons q_{bb}(C) and q_{cc}(C) values from Table II are shown in Figure 3 together with the analogous values for B and BH$^+$ from Table V of ref 2. Since all of the calculations were done with the same, reasonably large, basis set the values of the one-electron properties should be quite accurate in all four systems. The trends suggested by Figure 3 should consequently be valid to the extent that the neglect of geometry reoptimization does not cause appreciable difference in **q**(C). (To indicate the dependence on geometry changes the values for $R(C_1C_2) = 1.395$ Å and $\angle H_1C_1H_7 = 109.47°$ [2] are −0.032, −0.365, −0.188, and −0.443 for q_{bb} and −0.073, −0.409, −0.121, and −0.413 for q_{cc} at C_1, C_2, C_3, and C_4, respectively, for BH$^+$. The percentage changes compared with those in Figure 3 are seen to be largest for C_1 and C_3 but are expected to be considerably smaller for T and TH$^+$ since the geometric parameters are undoubtedly closer to equilibrium.)

The most striking feature of Figure 3 is that the TH$^+$ and BH$^+$ field gradients (also the C_2 rotation angles) are nearly the same for the ring carbon atoms. This near equivalence is even closer than that between the values at C_2, C_3, and C_4 in T and B. There is a large increase in q_{bb} and q_{cc} at C_4 going from T to TH$^+$ indicating increased positive charges. Another interesting feature is that the rotation angle at C_{4M} in T is reduced such that the principal field gradient axes in TH$^+$ point nearly along the C_4–C_{4M} bond instead of being skewed toward H$_4$Ml. This suggests that the effect of hyperconjugation in TH$^+$ is to delocalize the charge distribution into a more or less σ–π form that appears to have C_{2v} symmetry, as well as to render the sites ortho and para to the site of protonation considerably more positive than the meta positions. The para position is made more positive in TH$^+$ than in BH$^+$ while the ortho positions are changed by nearly the same amount. These effects are qualitatively what is observed in the population analysis comparisons (see below).

The comparisons among the individual contributions to the
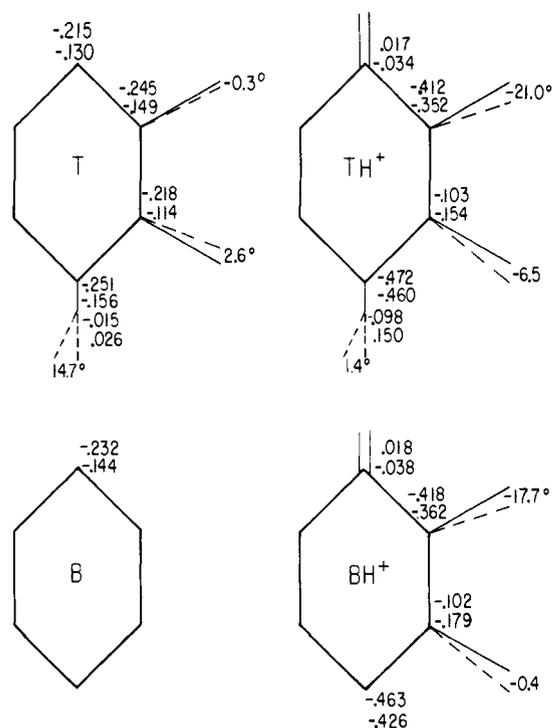
Figure 3. Electric field gradients in atomic units at unique carbon atoms (cf. Figure 4) for toluene (T), toluenium (TH$^+$), benzene (B), and benzenium (BH$^+$). The upper value at each center is q_{bb} and the lower q_{cc} (cf. Table II). The angles indicate the deviation of the principal axis system from the C–H bond direction in the plane of the ring (C_2 and C_3) and perpendicular to this plane (C_{4M}). B and BH$^+$ values are taken from Table V of ref 2.

field gradients may be made by examining Table II and Table V of ref 2. Whereas changes in the σ contributions are generally small (with the exception of C_4) the π contributions at C_1
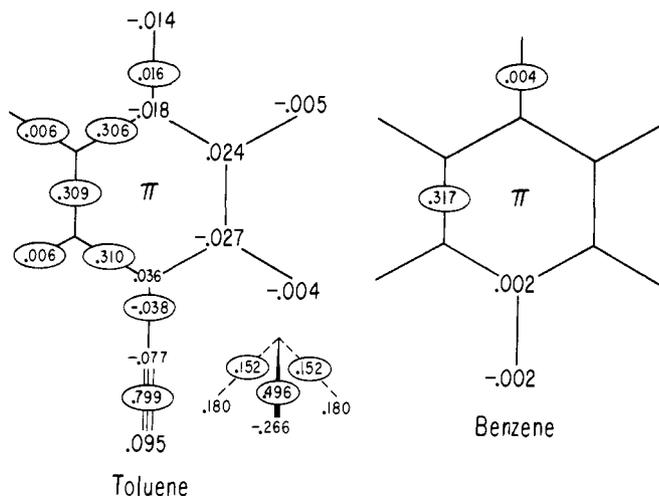
Figure 4. Computed π and quasi-π charges and (encircled) overlap populations in toluene and benzene.

Table III. Nuclear–Electron Potentials and Charge Densities at the Carbon and Hydrogen Nuclei of Toluene (T) and Toluenium (TH^+)[a]

Center		Φ	$\Phi(elec)$[b]	$\delta(r-A)$
T	C_1	-14.735	-25.414	122.531
TH^+		-14.521	-25.333	122.363
T	C_2	-14.731	-25.529	122.550
TH^+		-14.491	-25.461	122.693
T	C_3	-14.737	-26.028	122.539
TH^+		-14.543	-25.959	122.510
T	C_4	-14.725	-26.823	122.543
TH^+		-14.488	-26.696	122.754
T	C_{4M}	-14.729	-23.909	122.358
TH^+		-14.558	-23.828	122.362
T	H_1	-1.109	-11.206	0.447
TH^+		-0.868	-11.500	0.415
TH^+	H_7	-0.868	-11.500	0.415
T	H_2	-1.107	-11.319	0.447
TH^+		-0.897	-11.313	0.439
T	H_3	-1.107	-11.932	0.447
TH^+		-0.920	-11.857	0.436
T	H_{4M1}	-1.115	-10.910	0.435
TH^+		-0.928	-10.807	0.419
T	H_{4M2}	-1.116	-10.989	0.436
TH^+		-0.944	-10.901	0.427

[a] All values are in atomic units. [b] The electronic contribution to Φ is equivalent to the average diamagnetic shielding constant σ_{av}[d].

Table IV. Expectation Values of Powers of Coordinates with Origin at the Center of the Ring for Toluene (T) and Toluenium (TH^+)[a,b]

Property	T	TH^+
R^{-1}	0.157	0.367
	16.277	16.357
	-13.731	-13.692
	-2.390	-2.298
Z	-0.129	-0.045
	-46.818	-42.087
	26.711	34.517
	19.978	7.524
X	0.012	0.031
	0.000	0.000
	0.956	0.838
	-0.944	-0.807
R^2	-92.745	-68.947
	667.473	691.193
	-618.052	-612.968
	-142.166	-147.172
X^2	-35.211	-30.933
	5.867	11.173
	-20.714	-21.892
	-20.364	-20.213
Y^2	-28.732	-22.670
	196.854	196.854
	-198.201	-194.712
	-27.385	-24.812
Z^2	-28.802	-15.345
	464.752	483.166
	-399.137	-396.364
	-94.417	-102.147
XZ	-0.033	-0.205
	0.000	0.000
	-5.777	-4.678
	5.744	4.473

[a] The four entries for each property correspond to the total and its breakdown in terms of nuclear, σ, and π contributions. All entries are in atomic units. [b] Two misprints in Table VI of ref 2 are noted here. The value of the σ contribution to R^2 of C_6H_6 should be 394.766 and the σ contribution to Z^2 of $C_6H_7^+$ should be -288.042.

and C_{4M} show a substantial increase and at C_2 and C_4 a similar decrease in the cc component. The π contributions to q_{cc} (C_3), meta to the site of protonation, are nearly the same for T and TH^+. At C_1 the nuclear contribution is quite large for q_{bb} (Table II) and is mostly balanced by the σ contribution so that the net increase of about 0.2 au may be attributed to the change in q_{bb}^π.

The nuclear–electron potentials, diamagnetic shielding constants, and charge densities at the C and H nuclei are listed in Table III. As was true in the case of B and BH^+ these properties are much less sensitive to the presence of the added proton than are the field gradients.

The expectation values of powers of r are given in Table IV. The breakdown in terms of nuclear, σ, and π contributions again appears to attribute the largest changes in the charge distribution to the π electrons. The fact that there is a non-vanishing dipole moment in toluene makes it somewhat more difficult to compare with the $B-BH^+$ results, but it is worth

noting that the terms contributing to R^{-1} (ref 2, Table VI) are quite close to those in Table II. The reduction of Z from -0.129 to -0.045 due to the decrease in the π contribution supports the conclusion that TH^+ takes on a more symmetrical electronic charge distribution. Also the electronic contributions to R^2 (760.2 for T and 759.9 for TH^+) indicate that, as was true for B and BH^+, the protonation has only a small effect on the overall size of the molecule.

The computed proton affinity of toluene is 0.3154 au (8.582 eV or 197.9 kcal/mol), 9 kcal/mol greater than for computed benzene.[2] The experimental difference is 7.2 kcal/mol.[3]

Hyperconjugation, Population Analysis, and Toluene Dipole Moment

Ignoring the slight $\sigma-\pi$ interactions, a population analysis of σ and π and total MO populations was made in the usual way. The principal results (including overlap populations only for adjacent atoms) are displayed in Figures 4–7. In addition, the major overlap populations between nonadjacent atoms, and between H atoms in the CH_2 and CH_3 groups, are shown in Table V. These are large enough to make very appreciable negative contributions to the total bonding. Figure 4 for the π populations in toluene is in moderate agreement, as to charges on the ring atoms, with the results of a previous minimal-basis calculation.[4b] For the total population, the agreements[4a] (see Figure 5) are only qualitative.

Comparing benzene[2] with toluene, the charge distribution

Table V. Overlap Populations Exceeding 0.01 in Magnitude

Atoms[a]	Toluene			Toluenium		
	σ	π	Total	σ	π	Total
H1–H7				0.058	−0.126	−0.068
H1–C2 (4)	−0.080	−0.001	−0.081	−0.066	−0.006	−0.072
C_1–C_3 (2)	−0.098	−0.044	−0.142	−0.056	0.002	−0.054
C_1–C_4 (2)	−0.041	−0.046	−0.087	−0.048	0.009	−0.040
C_2–C_5 (2)	0.016	−0.053	−0.037	0.026	−0.033	−0.006
C_2–C_6	−0.145	−0.027	−0.171	−0.172	−0.053	−0.225
C_2–C_4 (2)	−0.128	−0.030	−0.158	−0.124	0.026	−0.099
C_3–C_5	−0.174	−0.015	−0.189	−0.154	−0.006	−0.160
C_3–C_6 (2)	0.016	−0.053	−0.037	0.026	−0.033	−0.006
H_2–C_1 (2)	−0.089	0.000	−0.089	−0.073	−0.000	−0.073
H_2–C_3 (2)	−0.085	0.000	−0.086	−0.051	0.001	−0.049
H_3–C_2 (2)	−0.084	−0.000	−0.084	−0.064	−0.004	−0.068
H_3–C_4 (2)	−0.084	−0.000	−0.084	−0.071	0.004	−0.067
H_3–C_{4M} (2)	−0.015	0.000	−0.015	−0.011	−0.005	−0.016
C_1–C_2 (2)	0.651	0.306	0.958	0.526	0.071	0.597
C_2–C_3 (2)	0.677	0.309	0.986	0.723	0.380	1.103
C_3–C_4 (2)	0.715	0.310	1.024	0.631	0.190	0.821
C_3–C_{4M} (2)	−0.078	−0.013	−0.091	−0.067	−0.012	−0.079
C_4–C_{4M}	0.297	−0.038	0.259	0.298	−0.052	0.246
C_3–H_{4M1} (2)	0.005	−0.024	−0.019	−0.000	−0.019	−0.020
C_3–H_{4M2} (2)	−0.020	0.011	−0.009	−0.014	0.015	0.001
H4M1–H4M2 (2)	0.031	−0.086	−0.055	0.028	−0.058	−0.030
H4M2–H4M3	−0.094	0.044	−0.049	−0.080	0.034	−0.046

[a] See Figure 2 for atom numberings. For most of the populations given, there is a second equivalent and equal overlap of two other atoms. The number of such equal overlaps is given in parentheses.
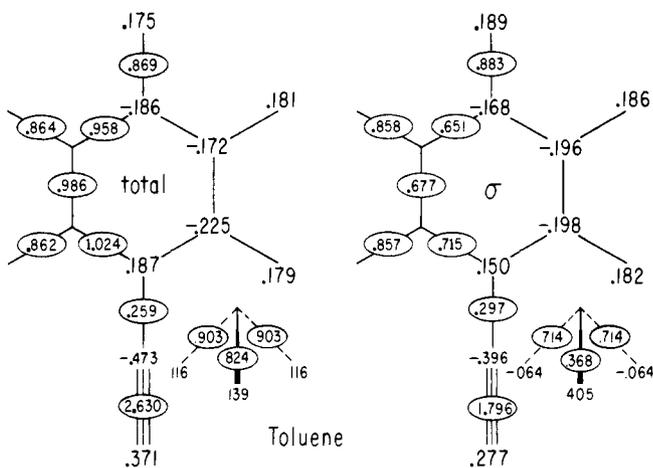
Figure 5. Computed total and σ charges and (encircled) overlap populations in toluene, omitting C_1C_3, C_1C_4, H_1H_7, etc., overlap terms.

Figure 6. Comparison of computed π and quasi-π charges and (encircled) overlap populations in toluenium and benzenium.

(Figures 4 and 5) shows increased negative charges, especially for π electrons, on the carbon atoms ortho and para to the methyl group in toluene. This is in accordance with the experimentally known ortho–para directing power of the methyl group in electrophilic substitutions. Note, however, that the negative charges are larger in the ortho than in the para positions.

The modified charge distributions of the ring carbon atoms in toluene as compared with benzene can be attributed to the combined inductive and hyperconjugative effects of the methyl group. The nature of the weak (sacrificial) hyperconjugation can be seen from the array of coefficients in Table VI. Hyperconjugation is shown by the fact that each of the a' π and quasi-π MOs, although predominantly localized, nevertheless extends to some extent throughout the molecule. For example, 12a' is predominantly a CH_3 MO, but is strongly attached to

the ring atom C_4, and extends weakly to the other ring carbon atoms. On the other hand, 14a' and 16a' are primarily ring MOs, but are distinctly antibonded to the CH_3 group. It is a necessary corollary of the variation theorem that the net delocalization effect of hyperconjugation is to increase total bonding. However, the overall computed π overlap population of −0.038e between atoms C_4 and C_{4M} (see Figure 4) raises a question. Possibly it is an artifact due to the fact that the population analysis procedure used cannot be trusted quantitatively. Or perhaps it is a valid result: it is not incredible that hyperconjugation involves a small net antibonding effect between C_4 and C_{4M} even though its total effect must be to strengthen the molecular binding.

Comparing toluenium with toluene, hyperconjugation is much stronger in the former. A new feature in toluenium is the

Table VI. Main Coefficients of Hyperconjugated MOs

		Toluene				Toluenium			
		12a′	14a′	9a″	16a′	12a′	14a′	16a′	9a″
ϵ, hartree		−0.575	−0.487	−0.335	−0.326	−0.801	−0.745	−0.612	−0.539
H_1, H_7	s					±0.194	∓0.061	±0.090	0.000
	s					±0.092	∓0.072	±0.078	0.000
	s					±0.028	∓0.024	±0.066	0.000
						B(0.525)	B(0.046)	B(0.104)	
C_1	p_x	0.034	0.206	0.000	−0.298	0.378	−0.102	0.137	0.000
	p_x	0.018	0.124	0.000	−0.213	0.217	−0.063	0.098	0.000
	p_x	0.004	0.031	0.000	−0.095	0.037	0.003	−0.049	0.000
		b(0.003)	B(0.110)	b(0.004)	B(0.188)	B(0.092)	a(−0.001)	a(−0.023)	b(0.003)
C_2, C_6	p_x	0.045	0.198	±0.259	−0.139	0.123	0.003	−0.112	±0.252
	p_x	0.024	0.119	±0.181	−0.098	0.058	0.007	−0.081	±0.183
	p_x	0.003	0.027	±0.079	−0.046	0.004	−0.004	−0.000	±0.059
		b(0.007)	B(0.105)	B(0.297)	A(−0.100)	b(0.019)	a(−0.002)	B(0.079)	B(0.283)
C_3, C_5	p_x	0.080	0.177	±0.263	0.165	0.077	0.064	−0.244	±0.276
	p_x	0.044	0.105	±0.188	0.116	0.043	0.034	−0.167	±0.206
	p_x	0.013	0.027	±0.080	0.059	0.005	−0.006	−0.047	±0.061
		b(0.024)	B(0.061)	b(0.005)	B(0.220)	b(0.012)	b(0.006)	B(0.165)	b(0.005)
C_4	p_x	0.147	0.143	0.000	0.293	0.069	0.140	−0.226	0.000
	p_x	0.083	0.091	0.000	0.219	0.041	0.083	−0.151	0.000
	p_x	−0.002	0.024	0.000	0.083	0.004	0.009	−0.035	0.000
		B(0.092)	a(−0.043)		A(−0.087)	b(0.007)	B(0.073)	A(−0.131)	
C_{4M}	p_x	0.371	−0.140	0.000	−0.083	0.056	0.379	0.157	0.000
	p_x	0.178	−0.080	0.000	−0.054	0.022	0.198	0.107	0.000
	p_x	0.048	−0.026	0.000	−0.026	0.006	0.034	0.049	0.000
		B(0.602)	B(0.124)		B(0.075)	b(0.011)	B(0.595)	B(0.158)	
H_{4M1}	s	0.245	−0.091	0.000	−0.080	0.033	0.231	0.117	0.000
	s	0.148	−0.063	0.000	−0.080	0.020	0.129	0.069	0.000
	s	0.049	−0.024	0.000	−0.050	0.002	0.034	0.010	0.000
		(−0.053)	(−0.015)		(−0.017)	(−0.001)	(−0.046)	(−0.011)	
H_{4M2}, H_{4M3}	s	−0.114	0.064	±0.002	0.040	−0.016	−0.125	−0.058	∓0.003
	s	−0.076	0.043	∓0.004	0.034	−0.011	−0.072	−0.036	±0.004
	s	−0.020	0.021	∓0.009	0.021	0.002	−0.022	−0.012	±0.003
		(0.026)	(0.012)		(0.008)		(0.027)	(0.007)	

[a] The letters B, A, b, or a indicate large (B, A) or small (b, a) bonding or antibonding between adjacent atoms or groups (H_2, H_3); corresponding overlap populations in each case are given in parentheses. In particular, B after C_{4M} refers to bonding to the quasi-π group orbital $\alpha(H_{4M1})$ − $\beta(H_{4M2} + H_{4M3})$. Interhydrogen overlap populations in the CH_3 group are also given in parentheses.
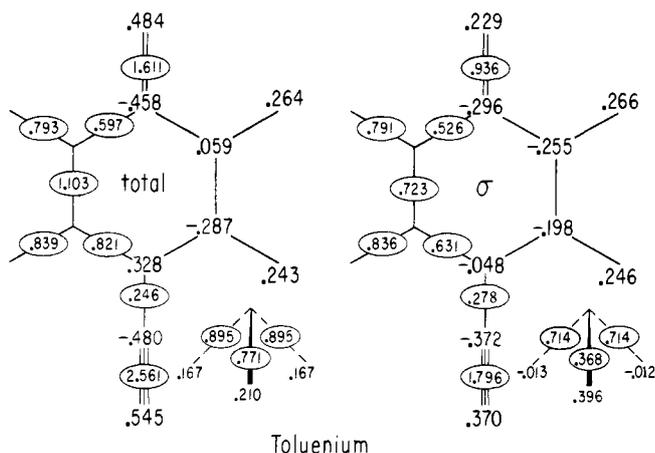
Figure 7. Computed total and σ charges and (encircled) overlap populations it toluenium, omitting C_1C_3. C_1C_4, H_1H_7, etc., overlap terms.

advent of the CH_2 group and its hyperconjugation. Although in the resonance structures of Figure 1 there is a quinoid structure linking the hyperconjugation of the CH_2 and CH_3 groups through the ring, in Table VI it is seen that of the π-quasi-π MOs, the deepest, 12a′, is largely confined to CH_2 hyperconjugation but 14a′ largely to CH_3 hyperconjugation. However, 16a′ involves hyperconjugation with both CH_2 and CH_3 groups, but with antibonding between both of these and

the ring. The 9a″ MO is only minutely affected by hyperconjugation.

As in benzenium vs. benzene, but somewhat more so (see the overlap populations in Figures 4–7), the bonding of carbon atoms C_2, C_3 and C_5, C_6 is strongly increased, and that for C_1C_2, C_1C_6 and C_4C_3, C_4C_5 much decreased, in toluenium vs. toluene, for both σ and π bonds. In toluene vs. benzene, the changes are much smaller. Consideration of the overlap populations in Table V indicates that small changes (as in benzenium vs. benzene[2]) are needed in some of the internuclear distances in the model assumed in the calculations.

Examination of the computed gross charges (Figures 5 and 7) in toluenium vs. toluene indicates that the charge of the added proton goes predominantly to the CH groups of atoms C_2 and C_6 (meta to the CH_3 group), and to a lesser extent to C_4 and the CH_3 group. The computed changes in gross populations are +0.309e for the combined charge of the two H atoms of the CH_2 group, −0.272e for the carbon atom of the CH_2 group (C_1), +0.314e for each of the CH groups belonging to carbon atoms C_2 and C_6, +0.02e for each of the CH groups belonging to carbon atoms C_3 and C_5, +0.141e for C_4, and +0.167e for the CH_3 group. Although the population analysis computation cannot be trusted quantitatively, these computed effects probably give a qualitatively correct picture of the change in charge distribution from toluenium to toluene. These trends may be compared with those for the electric field gradients shown in Figure 3.

Our computed dipole moment (Table IV) of toluene is

−0.130 au (−0.330 D) in the plane, together with a small component (0.031 D) perpendicular to the plane as expected for the model we used. The direction is as if the structure is $CH_3{}^+C_6H_5{}^-$, in agreement with the conclusion of earlier writers. The magnitude agrees with the experimental value of 0.36 D.[4b] On the other hand, our *population analysis* makes the CH_3 group total population *negative* by 0.102e (see Figure 5), even though the π part is +0.018e (Figure 4). While it seems possible that this effect is an artifact of the imperfection of the population analysis procedure, an examination of Figure 5 indicates that it may not be inconsistent with the charge distribution in the molecule. It seems possible that the polarities in the charge distribution in the ring can account for the overall direction of the dipole moment in spite of a negative CH_3 group.

References and Notes

(1) To whom correspondence should be addressed.
(2) W. C. Ermler, R. S. Mulliken, and E. Clementi, *J. Am. Chem. Soc.*, **98**, 388 (1976).
(3) J. L. Devlin III, J. F. Wolf, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **98**, 1990 (1976).
(4) (a) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 2191 (1970); (b) W. J. Hehre, L. Radom, and J. A. Pople, *ibid.*, **94**, 1496 (1972).
(5) See, for example, C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953).
(6) H. D. Rudolph, H. Dreizler, A. Jaescke, and P. Windling, *Z. Naturforsch. A*, **22**, 940 (1967).

A Theoretical Study Concerning Mechanisms of the Molecular Rearrangement of Carbonyl Compounds to Oxacarbenes in the Lowest Triplet State

Julianna A. Altmann,*[1] I. G. Csizmadia,[1] Michael A. Robb,[2] Keith Yates,[1] and Peter Yates[1]

Contribution from the Departments of Chemistry, University of Toronto, Toronto, Ontario, Canada, and Queen Elizabeth College, London, England. Received April 16, 1977

Abstract: Nonempirical LCAO-SCF-MO calculations, applying a spin-restricted partitioned Hartree–Fock (PHF) method to open shells, have been carried out to investigate the effect of both basis set size and alkyl substitution on the mechanistic preference of the rearrangement of triplet carbonyl compounds to triplet oxacarbenes, as modeled by formaldehyde. Results suggest that the preference for the concerted pathway is independent of the size of the basis set. Substitution of an alkyl group for the migrating hydrogen changes the mechanistic preference from a concerted pathway to a diradical process. The relevance of these results to the rearrangement of cyclic ketones is discussed.

Introduction

The name "oxacarbene" denotes a molecule that has an oxygen attached to a carbenic center. The formation of an oxacarbene as a reactive intermediate was first postulated by Yates and Kilmurry[3] in connection with the photochemical conversion of cyclocamphanone (1) to ring-expanded acetals

1

2 a, R = CH₃
  b, R = C₂H₅
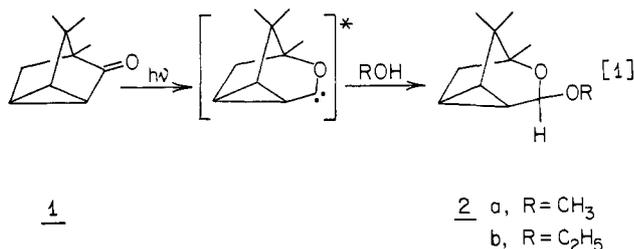
2a and **2b**, respectively. Since this first report a considerable amount of research effort has been devoted to the study of this reaction. It was found that the formation of ring-expanded products is dependent on various structural features. There is a dichotomy[4] in both the nature of the reactive excited states involved in this process and its mechanism.

Based on experimental evidence, it appears that some cyclic ketones react via their $n\pi^*$ singlet states,[4,5] whereas others react via their $n\pi^*$ triplet states.[6]

Two mechanistic alternatives have been proposed to account for the photochemical transformation of cyclic ketones to oxacarbenes. One involves an α-cleavage of the carbonyl compound (3) to give a diradical species (4) which recombines at
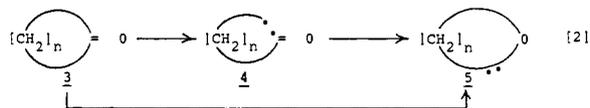
oxygen to form the oxacarbene (5) (dissociation-recombination or diradical mechanism), and the other involves the formation of 4 directly from the excited ketone (concerted mechanism).

We have recently carried out a systematic ab initio study of the carbonyl–oxacarbene interconversion. In the first part of the study we investigated two distinct photochemical pathways (i.e., singlet and triplet) using formaldehyde as a model ketone. We reported[7] that, according to our results, a concerted rearrangement in the triplet state is expected to be favored.

The present report is concerned with the investigation of the effect of both the size of the basis set and alkyl substitution on the mechanistic preference of the rearrangement:

Computational Details

All the computations were of the nonempirical LCAO-