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RELATIVE ENERGIES OF SUBSTITUTED BENZENE VALENCE ISOMERS

ARTHUR GREENBERG*
Department of Chemical Engineering and Chemistry, New Jersey Institute of Technology, Newark, NJ 07102, U.S.A.

and

JOEL F. LIEBMAN*
Department of Chemistry, University of Maryland Baltimore County, Catonsville, MD 21228, U.S.A.

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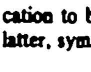
Abstract—*Ab initio* calculations employing the STO-3G basis set are used to obtain the relative energies of the benzene valence isomers and some selected monosubstituted derivatives. We find that 3,3'-bicyclopropenyl, the least stable of the five $(CH)_6$ examined, is slightly more stable in the *anti* conformation than the *gauche* ($\phi = 45°$) conformation in agreement with experiment. Substituents are calculated to produce significant changes in the relative energies of the benzene valence isomers. The ground-state isomerization of 1-Dewar benzenecarbinyl cation to benzyl cation is more exothermic than the aromatization of Dewar benzene, but is, in contrast to the latter, symmetry-allowed.

As part of a continuing effort to assess the effects of substituents upon stabilities of strained organic molecules,[1-3] an investigation of derivatives of the benzene valence isomers 1–5 is of special interest. These compounds have nine unique carbon environments and the stabilizing or destabilizing effects of substituents at these positions can be evaluated through direct comparison of the energies of the isomeric $(CH)_6$ and the analogous derivatives. Furthermore, the photo-isomerizations of benzene to other $(CH)_6$ (albeit in very low yield)[4] their surprising thermal stabilities,[5-9] and ready aromatizations in the presence of metal catalysts[10] recall some of the characteristics of light storage-latent heat conversion systems.[11,12] Thus, the effects of substituents upon the relative stabilities of $(CH)_6$ may find eventual application in studies of other more efficient light storage molecular systems.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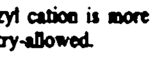

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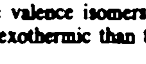

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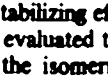
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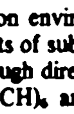

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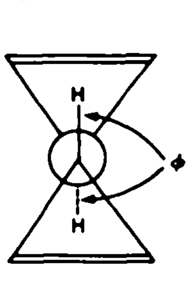
Methodology. Newton *et al.* have calculated the properties of 1–4 at both the STO-3G and 4-31G levels.[13,14] We have employed their calculated geometries for 1–4 as the basis for the current investigation which was performed with the GAUSSIAN 70 series of programs[15] at the STO-3G level.[16] The geometry of 5 was obtained through combination of the calculated geometry of cyclopropene,[17] experimental geometry of bicyclopropyl,[18-20] and limited geometry optimization as discussed later. Monosubstituted species were generated by simply replacing H by various substituents (Li, BH_2, CH_2^+, F, OLi) having specified structural parameters[21] and leaving the carbocyclic framework invariant. Comparison of the energies of substituted derivatives and their hydrocarbon analogues in order to obtain the corresponding aromatization energies is an isodesmic[22] approach which largely cancels inadequacies in calculations of strain energies and the absence of electron correlation.

Benzene valence isomers. Table 1 lists total energies (hartrees) and relative energies (kcal/mole) of 1–4 obtained by Newton *et al.* at both the STO-3G[13] and 4-31G[14] levels. Additionally, the total energies and relative energies calculated for 3,3'-bicyclopropenyl (5) in its *anti* (5a, $\phi = 180°$), *syn* (5b, $\phi = 0°$), and *gauche* (5c, $\phi = 45°$) conformations[19] are tabulated. The geometry of the cyclopropene ring in 5 has been taken as equal to that calculated[17] for cyclopropene itself, the C3–C3' bond is found to be equal to 1.51 Å and the $H_3C_3C_3'$ angle equal to 114.7° (assumed to be bisected by the appropriate cyclopropene molecular plane) following a limited geometry search employing the reported geometries of bicyclopropyl as a starting point. Bicyclopropyl is itself a complex conformational problem known to consist of almost equal fractions of two conformers:[18-20] an *anti* structure (analogous to 5a) having a rotational amplitude of about ±80° and a *gauche* structure (analogous to 5c) having a rotational amplitude of about ±18°.

In Table 1 are listed experimental enthalpy differences between 1–4 (actually the hexamethyl derivatives) as well as an estimate for the relative enthalpy of 5. An amusing feature is that the STO-3G energies are in



5a ($\phi = 180°$)
5b ($\phi = 0°$)
5c ($\phi = 45°$)

Table 1. Total energies (au) and relative energies (kcal/mole) por benzene valence isomers (**1**–**5**) calculated with the STO-3G and 4-31G basis sets

Isomer	STO-3G		4-31G		Rel. Energy
	Total Energy (hartrees)	Rel. Energy (kcal)	Total Energy (hartrees)	Rel. Energy (kcal)	(Experimental) (kcal)
Benzene (**1**)	-227.89128[a]	0	-230.3774[b]	0	0
Dewar Benzene(**2**)	-227.76568[a]	78.7	-230.2145[b]	102.2	59.5[c]
Benzvalene(**3**)	-227.78248[a]	68.2	-230.2108[b]	104.5	67.5[c]
Prismane(**4**)	-227.74379[a]	92.5	-230.1383[b]	149.9	91.2[c]
3,3′-Bicyclopropenyl					119 [d]
anti conformer(**5a**)	-227.66341	142.9	-230.1312	154.4	
syn conformer(**5b**)	-227.66093	144.4			
gauche (45°) conformer(**5c**)	-227.66251	143.4			

a. See reference 13

b. See reference 14

c. This actually refers to the hexamethyl series; see J.F.M. Oth, Angew. Chem., Int. Ed. Engl., 7, 646 (1968).

d. Estimated as follows:
$2\,\Delta H_f^{\circ}(\text{cyclopropene}) + \Delta H_f^{\circ}(\text{bicyclopropyl}) - 2\,\Delta H_f^{\circ}(\text{cyclopropane})$

surprisingly good quantitative agreement with experiment, although benzvalene is calculated to be lower in energy than Dewar benzene contrary to experiment. This can only be attributed to fortuitous cancellation of errors, and the 4-31G data, though seemingly poorer quantitatively than the STO-3G results, properly reproduce the order of stabilities of **1**–**5**.

3,3′-Bicyclopropenyl has received relatively little attention compared to the other four $(CH)_6$. Although the parent compound has not been reported, dimethyl derivatives are known,[23–25] and the first known derivative of a benzene valence isomer was in fact hexaphenyl-3,3-bicyclopropenyl.[5] One unanticipated feature calculated for 3,3′-bicyclopropenyl and its derivatives is a dramatic long-range interaction between the two π orbitals in the *anti* as well as *syn* isomers.[26] This has been confirmed experimentally[27] and will be discussed elsewhere.[28]

Monosubstituted benzene valence isomers (*substituents* Li, F, BH_2, OLi). Substituents can dramatically alter the stabilities of strained and unsaturated organic linkages relative to saturated analogues.[2] Sigma donation by a substituent is stabilizing, sigma withdrawal is destabilizing, pi withdrawal and most cases of pi release are stabilizing. Thus, an Li substituent stabilizes unsaturated (strained) systems such as ethylene and cyclopropane predominantly through σ release although a small fraction of stabilization is associated with π withdrawal; for BH_2 stabilizing σ and π effects are equal in magnitude; for OMe, σ and π effects oppose each other with the latter dominating and providing net stabilization; $\overset{+}{N}H_3$, a virtually pure σ withdrawer, destabilizes unsaturated and strained systems.[2] Within a series of hydrocarbons the effects are usually greatest for the most unsaturated units.

Table 2 lists STO-3G calculated total energies and relative energies for a number of substituted C_6H_5X. Originally, we had hoped to calculate isomeric $C_6H_5O^-$ since the σ-releasing, π-releasing O^- substituent has been calculated to provide strained and unsaturated molecules with substantial stabilization. The photochemical transformations, if any, of phenoxide or more likely the thermally-induced rearrangements of, e.g. 1-benzvalenoxide would be of particular interest if the substituents were to introduce substantial changes in relative energies of isomeric $C_6H_5O^-$. Unfortunately, most of the calculations of these larger anionic species diverged. Lithium alkoxides (Table 2, column 5) show very small effects compared to those anticipated for the anions since the negative charge is substantially more delocalized in the latter. Similarly, we were interested in calculations of isomeric $C_6H_5BH_3^-$, since some photochemistry has been described for tetraphenylborate.[29] However these calculations also diverged.

Some of the calculated substituent effects in Table 2 are fairly substantial. They may be capable of altering the photochemical behavior of some of the isomers listed. The relative magnitudes of the effects are in line with, and indeed predictable by analogy to, smaller substituted molecules (e.g. 1-lithiobicyclobutane vs 2-lithiobicyclobutane).[2] In a related study,[30] we find that CF_3-derivatives of the benzene valence isomers have about equal energy relationships when compared to the corresponding $(CH)_6$.

Benzyl cation and its valence isomers. Substitution of a CH_2^+ group for H in a benzene valence isomer can be likened to "lifting the latch on the paper cage holding an angry tiger",[31] since carbonium ion rearrangement pathways become available as a means of releasing energy. Table 2 lists calculated total energies (hartree) and relative energies (kcal/mole) for isomeric $C_6H_5CH_2^+$. The effects are large and dominated by the stabilization in benzyl cation.

One of the most interesting points to ponder is raised through comparison of the relative energies of 1-Dewar benzene carbinyl cation and benzyl cation. Resonance

Table 2. STO-3G total energies (hartrees) and relative energies (kcal/mole) of substituted benzene valence isomers

	X = H	X = Li		X = F		X = BH$_2$		X = OLi	
	Relative Energy (kcal/mole)	Total Energy (hartrees)	Rel. Energy (kcal/mole)	Total Energy (hartrees)	Rel. Energy (kcal/mole)	Total Energy (kcal/mole)	Rel. Energy (kcal/mole)	Total Energy (hartrees)	Rel. Energy (kcal/mole)
	0	-234.60103[a]	0	-325.34939[b]	0	-252.84219[a] (planar)	0	-308.54206	0
	78.7	-234.47498	79.1	-325.22237	79.7	-252.70981	83.0	-308.41225	81.4
		-234.48658	71.8	-325.22901	75.5	-252.71993	76.7	-308.42268	74.9
	68.2	-234.50709	58.9	-325.23652	70.9	-252.74250	62.5	-308.42948	70.6
		-234.49029	69.4	-325.23708	70.5	-252.72238	75.1	-308.42710	72.1
		-234.50447	60.4	-325.24141	67.8	-252.74013	64.0	-308.43307	68.3
	92.5	-234.45956	88.7	-325.20151	92.8	-252.70003	89.1	-308.39299	93.5
	142.9	-234.39909	126.6	-325.12022	143.8	-252.62208	138.0	-308.31670	141.3
		-234.36042	150.9	-325.12452	141.1	-252.60181	150.7	-308.31414	142.9

[a] These values are unpublished work of J.D. Dill, J.A. Pople, and P. von R. Schleyer ; J.D. Dill personal communication.

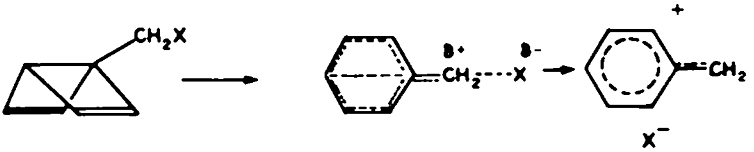
[b] W. J. Hehre, L. Radom and J. A. Pople, J. Amer. Chem. Soc., 94, 1496 (1972).

Table 3. Total energies (hartree) and relative energies (kcal/mole) of benzyl cation and valence isomers employing STO-3G basis set

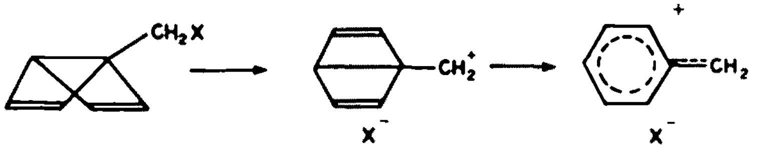
Cation	Total Energy (hartree)	Relative Energy (kcal/mole)
Benzyl	-265.65231[a]	0
1-Dewar benzenecarbinyl (gauche)	-265.47777	109.5
1-Dewar benzenecarbinyl (bisected)	-265.46462	117.7
2-Dewar benzenecarbinyl (idealized conjugated)	-265.51087	88.7
2-Dewar benzenecarbinyl (conj allylic)	-265.52139	82.1
1-benzvalenecarbinyl (gauche)	-265.50985	89.3
1-benzvalenecarbinyl (bisected)	-265.47396	111.8
2-benzvalenecarbinyl	-265.46657	116.5
3-benzvalenecarbinyl (idealized)	-265.53534	73.4
3-benzvalenecarbinyl (allylic)	-265.55352	62.0
prismanecarbinyl	-265.47417	111.7
3,3′-bicyclopropenyl-3-carbinyl (gauche)	-265.38671	166.6

[a] W.J. Hehre, Methods of Electronic Structure Theory, H.F. Schaefer, III (ed.), Plenum Publishing Corp., New York, 1977, pp. 277-331.

stabilization in the latter makes the aromatic specie substantially more stable relative to the Dewar benzene isomer than is the case for the (CH)$_6$ molecules. At the same time delocalization of the positive charge might provide 1-Dewar benzenecarbinyl cation with substantial resemblance to a distorted benzyl cation, perhaps requiring no barrier at all. Should that be the case, solvolysis of 1-Dewar benzenecarbinyl tosylate (or the like) should be anomalously rapid due to formation of a benzyl-like activated complex (Scheme 1). At the other



Scheme 1.



Scheme 2.

extreme, one might anticipate slow formation of a primary carbonium ion followed by rearrangement to benzyl cation in the manner of Scheme 2. Here, an interesting factor arises. While, the ground-state isomerization of Dewar benzene is "symmetry forbidden",[32] examination of Fig. 1, the correlation diagram for 1-Dewar benzenecarbinyl cation and benzyl cation, shows that the latter is "symmetry-allowed." This does not appear to us to be an artifact of reduced symmetry in the isomeric $C_6H_5CH_2^+$ relative to isomeric C_6H_6. Thus, thermal aromatization of 1-Dewar benzenecarbinyl cation should be faster and more exothermic than the aromatization of Dewar Benzene. The question of thermal access to electronically-excited benzyl cation enters at this point. Figure 1 shows that a transition from ground-state 1-Dewar benzenecarbinyl cation is symmetry forbidden while conversion to the doubly-excited state (occupancy of ψ_{26}) is symmetry-allowed. Given the energetics of the rearrangement, other pathways to excited-state benzyl cation might be feasible. It should be noted here that other workers have reported the photochemistry of triphenylcarbinyl (trityl) cations.[33] Similarly one wonders about the ability of bicyclo[3·2·0]heptatrienyl cations to generate electronically-excited tropylium cation.

Another possibility must also be considered. Given the propensity of 1-bicyclo[2·2·0]hexanecarbinyl derivatives to rearrange to form 1-norbornyl compounds,[34] one must also consider the possibilities summarized in Scheme 3. One would think that the 1-norbornadienyl cation should be even less stable than the 1-norbornyl cation due to

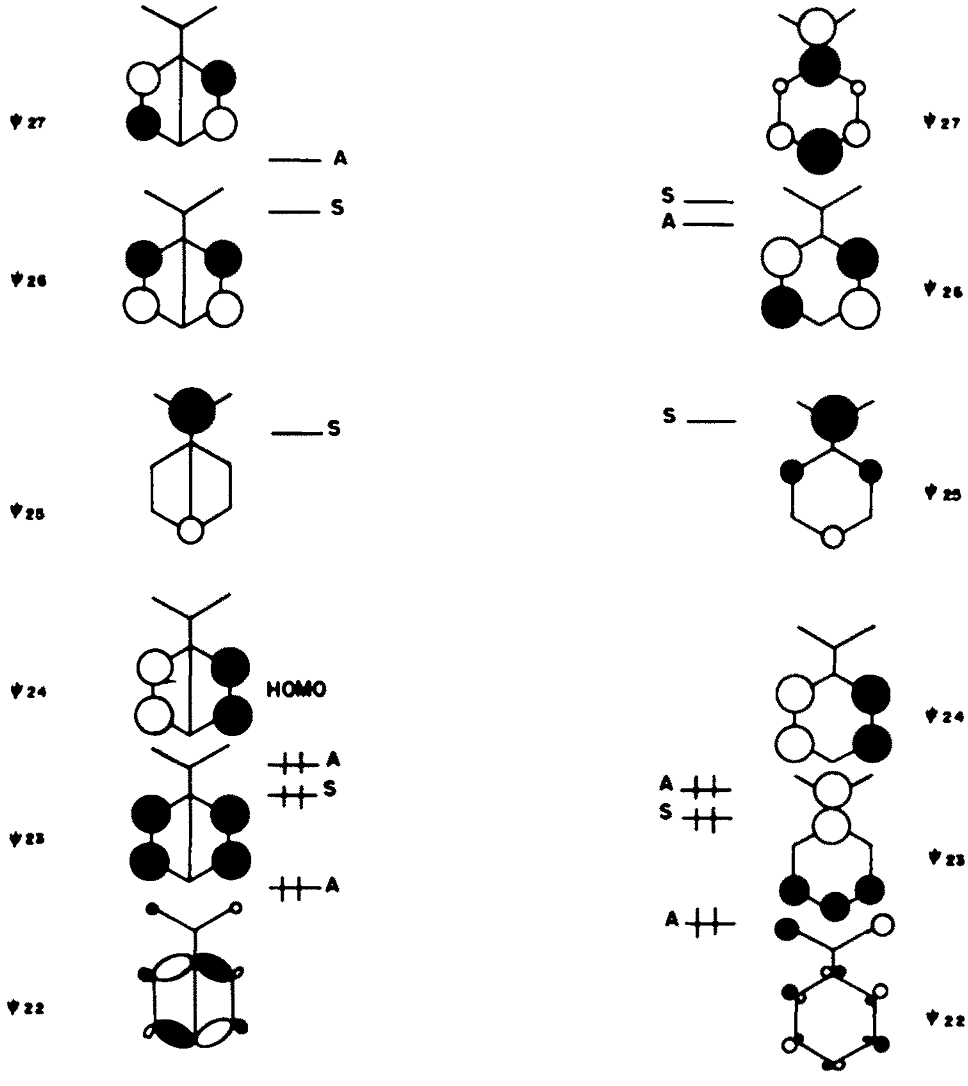
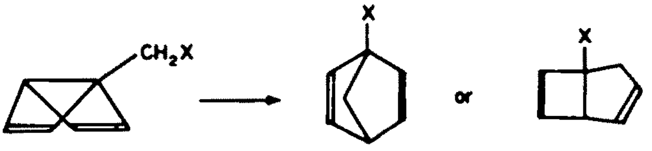


Fig. 1. Correlation of molecular orbitals of 1-Dewar benzenecarbinyl cation (*gauche*) and planar benzyl cation.



Scheme 3.

destabilizing inductive affects in the former and that the stability of benzyl cation should surely make this species more accessible.

Table 3 provides some additional noteworthy features. The rotational barrier calculated for 1-benzvalenecarbinyl cation is 22.5 kcal/mole, some 9.3 kcal less than for 1-bicyclobutylcarbinyl cation.[2] The cause of this effect is the unnaturally highly puckered geometry of the bicyclobutane ring in benzvalene. Calculations on "model bicyclobutane" having this geometry indicate that (a) it is higher in energy than bicyclobutane in its reported structure,[35] and (b) the highest occupied molecular orbital, which is π-like and localized between the bridgehead carbons[35] is of lower energy for the highly puckered "model bicyclobutane" representing the unit in benzvalene than for bicyclobutane itself. Thus, the stabilizing interaction of the π-like HOMO with the CH_2^+ substituent in its most favorable *gauche* conformation[3] is lessened for the highly puckered "model bicyclobutane" and the rotational barrier lowered. Another manifestation of the puckering of the bicyclobutane ring in benzvalene is the increased stabilization in going from an idealized 3-benzvalencarbinyl cation (CH_2^+ substituent, co-planar with the olefinic linkage, C_3–C_4 = 1.35Å; C_4–C_7 = 1.47Å) to a 3-benzvalenecarbinyl cation having an allylic system (C_3–C_4 = C_4–C_7 = 1.385 Å). The calculated stabilization is 11.4 kcal/mole, which may be compared with either the 4.9 kcal/mole stabilization on going from planar "3-propenyl cation" to allyl cation[2] or the stabilization of 6.6 kcal/mole in going from planar "3-propenyl" to allyl cation structures of 2-Dewar Benzenecarbinyl cation (Table 3). The extra stabilizing increment in the transformation to allylic 3-benzvalenyl carbinyl cation is attributable to some flattening of the bicyclobutane ring thus producing a geometry closer to that of free bicyclobutane. The rotational barrier calculated for 1-Dewar benzenecarbinyl cation is only 8.3 kcal/mole, reflecting the low p-character of the C_1–C_4 bond in Dewar benzene relative to the C_1–C_3 bond of bicyclobutane or the C_1–C_6 bond of benzvalene.

Summary. Substituents can have dramatic effects upon the relative energies of benzene valence isomers. These effects are predictable through reference to smaller model compounds such as fluoroethylene, lithiobicyclobutanes, etc. Substituents should play an analogous role in fine-tuning energy relationships between other isomeric systems such as quadricyclane-norbornadiene.

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[21] Structural parameters of substituents: C–Li, 2.01 Å; C–F, 1.37 Å; C–CH_2^+ (CH_2^+ assumed to be 120° trigonal), C–C, 1.47 Å, C–H, 1.10 Å; C–BH_2 (BH_2 assumed to be 120° trigonal), C–B, 1.57 Å, B–H 1.16 Å; C–OLi, C–OLi assumed to be linear, C–O, 1.41 Å, OLi, 1.432 Å, see J. D. Dill, P. von R. Schleyer, J. S. Binkley and J. A. Pople, *J. Am. Chem. Soc.* 99, 6159 (1977).

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