anisotropies cannot explain the small (in magnitude) anisotropy in isoprene relative to cyclopentadiene.

According to the above discussions, we conclude that the anisotropies in the ring molecules listed in Table V from cyclopentadiene to benzene must be described in terms of *both* local and nonlocal contributions. From the isoprene–cyclopentadiene study, the local effects and the ring current contribute roughly an equal amount to the anisotropy. If this is true in general, it lends support to the modified ring-current theories.[3-5]

We are trying to develop a set of local group anisotropies in order to determine with more confidence the magnitude of the nonlocal effects, but refinements, along with more data, are necessary. For example, in isoprene there is the possibility that the anisotropy might change depending on the location of the methyl group or that the methyl and methylene carbon atoms in isoprene and cyclopentadiene have a different anisotropy even though both carbon atoms have sp^3 hybridization. The first possibility is easy to test by measuring the anisotropies in *cis*- and *trans*-1,3-pentadiene. We are presently trying to do this, but the line strengths are extremely weak. As another example, the anisotropies of acrolein and crotonaldehyde would give the anisotropy of the methyl group. (The anisotropy for acrolein is very close to that for isoprene.[39]) But at the present time, we feel that these effects will be small (less than 5 units) and will not explain the factor of 2 between the anisotropies of isoprene and cyclopentadiene.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged. We would also like to thank J. Musher for some interesting comments on magnetic susceptibilities which stimulated much of the work in the present paper.

[39] R. C. Benson and W. H. Flygare, unpublished results.

Molecular Orbital Calculations on the 2-Phenylethyl → Phenonium Cation Transformation

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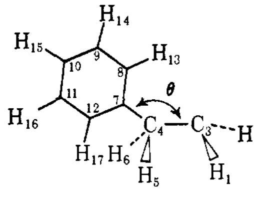
Contribution from the Department of Chemistry, East Tennessee State University, Johnson City, Tennessee 37601. *Received May 9, 1970*

Abstract: The reaction coordinate for the transformation, classical 2-phenylethyl → phenonium cation, has been mapped using CNDO/2 calculations. That the results of such calculations must be quantitatively grossly incorrect was shown by the results of similar calculations for the corresponding radical species. We show that CNDO/2 has a built-in bias for three-membered ring formation, at least for the Pople and Wiberg parametrizations. Extended Hückel calculations on the same problem give results which are the qualitative inverse of those of CNDO. However, known experimental data demonstrate that the EHT results are also quantitatively incorrect. Thus neither semiempirical calculation gives results which can be trusted.

The nature of the 2-phenylethyl cation remains a question of current interest.[2] To assist in the structural formulation, we have employed semiempirical molecular orbital calculations to construct the potential energy surface for the equilibrium

$$C_6H_5CH_2CH_2^+ \rightleftharpoons {}^+CH_2CH_2C_6H_5$$

Results would be most valid for the gas-phase reaction, but remain meaningful for the condensed phase provided that the solvation energy of species along the reaction coordinate does not change significantly. When this work was performed, the CNDO SCF MO treatment of Pople[3] seemed the best compromise between relevant quantum-mechanical completeness and computational manageability. Using parameters suggested by Wiberg,[4] the energy of the 2-phenylethyl cation was calculated as a function of the angle θ.



For every value of θ the geometry of the cation was optimized to minimize the *total* energy (electronic + nuclear repulsive). This optimization procedure was continued until all bond distances and angles were within 0.02 Å and 2°, respectively, of the structure corresponding to the absolute minimum energy geometry. Coordinates of the various nuclei were calculated sub-

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[1] All computational work was performed at the University of Connecticut. The basic program obtained from the Quantum Chemistry Program for Exchange was modified somewhat, including the addition of a subroutine for bond index calculations. Because the prediagonalization feature of the original program sometimes caused errors to mount, resulting in divergence in the SCF-iteration sequence, it was omitted in most calculations. Address correspondence to the author at Kraftco Corp., Research and Development Division, Glenview, Ill. 60025.

[2] P. v. R. Schleyer, *et al.*, *J. Amer. Chem. Soc.*, **91**, 4291, 4294, 4296, 4297, 7508 (1969); S. Winstein, *et al.*, *ibid.*, **90**, 6546 (1968); **91**, 4300 (1969); J. L. Coke, *et al.*, *ibid.*, **91**, 1154, 4284 (1969); R. J. Jablonski and E. I. Snyder, *ibid.*, **91**, 4445 (1969); J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968); G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969). For a viewpoint significantly different from those expressed above, see S. L. Loukas, M. R. Velkou, and G. A. Gregoriou, *Chem. Commun.*, 251 (1970), and references cited therein.

[3] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965); **44**, 3289 (1966).

[4] K. B. Wiberg, *J. Amer. Chem. Soc.*, **90**, 59 (1968).

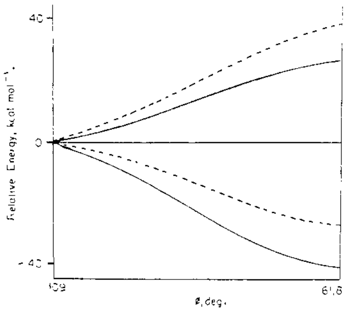


Figure 1. Angular dependence of the energy of the 2-phenylethyl cation (—) and radical (---) according to EHT (upper two curves) and CNDO (lower two curves) calculations.

ject to several geometric constraints imposed on the molecule. Firstly, the alkyl fragment (atoms 1-6) had a local plane of symmetry passing through C_3–C_4–C_7. Secondly, the planar aryl portion, with its local C_{2v} symmetry and the C_2 axis through C_7–C_{10}, was so constructed that bond lengths C_7–C_8, C_8–C_9 = C_9–C_{10}, and the angle C_8–C_7–C_{12} were the only independent parameters. (All aryl C–H bond lengths were assumed equal.) The angles C_8–C_9–C_{10} and C_9–C_{10}–C_{11} were made identical, which forced any change of the C_8–C_7–C_{12} angle to be reflected mainly in the C_7–C_8–C_9 angle. Bond angles and distances for structures with the extreme values of θ employed, and the total energy calculated for those structures, are given in Table I. Results are graphically displayed in Figure 1.

Table I. Optimized Geometrical Parameters for Open ("Classical") and Cyclic (Phenonium) 2-Phenylethyl Cations[a]

	Open	Cyclic
C_3–C_4	1.42	1.47
C_3–H_1	1.13	1.13
C_4–H_5	1.13	1.13
C_4–C_7	1.54	1.57
C_7–C_8	1.42	1.45
C_8–C_9, C_9–C_{10}	1.42	1.42
Aromatic C-H	1.12	1.12
$\angle H_1$–C_3–H_2	120	116
$\angle H_1$–C_3–C_4	120	117
$\angle C_3$–C_4–H_5	113	117
$\angle H_5$–C_4–H_6	111	116
$\angle C_3$–C_4–C_7 ($\equiv \theta$)	109	61.9
$\angle C_{12}$–C_7–C_8	120	116
$\angle C_7$–C_{12}–C_{11}	120	119.9
$\angle C_{12}$–C_{11}–C_{10}	120	122.1
E(cation), au	−60.3546	−60.5448

[a] Bond distances in ångströms, angles in degrees.

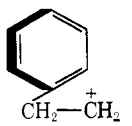
Bond indices[5] and charge densities for these structures and the "π-complex" structure (*vide infra*) are listed in Table II.

Table II. Bond Index–Charge Density Profiles for Cations

Atom no.	Open	Cyclic	"π complex"[a]
	Charge Density		
1	+0.109	+0.064	+0.066
3	+0.286	+0.058	+0.096
4	−0.040	+0.058	+0.019
5	+0.099	+0.064	+0.067
7	+0.073	+0.041	+0.031
8	+0.006	+0.113	+0.106
9	+0.027	−0.023	−0.021
10	+0.037	+0.134	+0.140
13	+0.025	+0.050	+0.053
14	+0.038	+0.058	+0.058
15	+0.039	+0.059	+0.058
$C_3 + H_1 + H_2$	+0.504	+0.186	+0.228
$C_4 + H_5 + H_6$	+0.158	+0.186	+0.153
Total alkyl portion	+0.662	+0.372	+0.381
$C_8 + H_{13}$	+0.031	+0.163	+0.159
$C_9 + H_{14}$	+0.065	+0.035	+0.037
$C_{10} + H_{15}$	+0.076	+0.193	+0.198
	Bond Index		
3–1	0.970	0.975	0.975
3–4	1.354	1.136	1.100
3–7	0.176	0.710	0.620
4–5	0.924	0.975	0.975
4–7	0.728	0.710	0.815
7–8	1.402	1.202	1.188
8–9	1.442	1.521	1.514
8–13	0.969	0.971	0.971
9–10	1.428	1.521	1.381
9–14	0.970	0.969	0.969
10–15	0.970	0.968	0.969

[a] The geometry of the π complex differs from that of the cyclic ion only in that $\angle C_4$–C_7–C_{10} = 180° in the former.

The results of these calculations may be summarized as follows. (1) The cyclic cation is considerably more stable than the open one (however, *vide infra*). Furthermore, the potential energy decreases continuously from the open ion to that of C_{2v} symmetry with no indication of local minima or maxima. This suggests the uselessness of referring to an open or "classical" 2-phenylethyl cation, for it has no significant energy barrier to surmount in its conversion to the cyclic or "nonclassical phenonium" ion, and is thermodynamically unstable relative to the latter. (2) Significant, but only *partial*, charge transfer to the aryl ring accompanies the open → cyclic ion transformation. Roughly two-thirds of the positive charge resides in the aryl portion (carbons and hydrogens) in the cyclic ion, mainly in the ortho and para positions, whereas one-third of the charge resides there in the open ion. (3) The major changes in bonding, as indicated by bond indices, are between C_3–C_1 and C_3–C_7. From the values of the table the C_3–C_1 bond in the cyclic cation seems quite close to a normal single bond with both carbons fairly strongly bonded to C_7. In qualitative terms this seems to indicate the phenonium ion is far more akin to a σ complex than a π complex. Or in valence bond terminology, it would appear that structure d is of minimal importance in the resonance hybrid. (4) The aryl group has an unusual low-frequency vibration equivalent to rocking about C_7, for calculations show that when C_4, C_7, and C_{10} are collinear as below, the energy rises by only 0.001 au.



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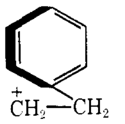

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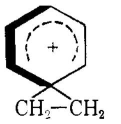

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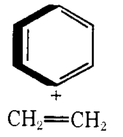
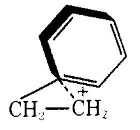


d



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(5) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); C. Trindle and O. Sinanoğlu, *J. Amer. Chem. Soc.*, **91**, 3940 (1969).

Chemically, the "picture" of this structure seems to be that of a π complex (but of a different type than contributing structure d above). However, the bond index–charge density profile belies this notion. No changes in bond index greater than 3% are calculated except for C_3–C_7 and C_4–C_7 where the change in symmetry is reflected. However, the *sum* of the latter bond indices changes less than 3%. Charge densities, particularly in the aryl ring, are virtually identical for the σ- and π-complex structures. In particular, most of the charge remains at the ortho and para positions, whereas for a π complex one might expect a more statistical distribution of charge.

That the energy difference between open and cyclic ion calculated by the CNDO method is quantitatively grossly incorrect is suggested by the following. Similar calculations on the 2-phenylethyl radical give a curve similar to that obtained for the cation, but with the cyclic radical favored over the open one by an amount less than that for the respective cations. However, experimental evidence[6] clearly shows the radical $PhCH_2CH_2\cdot$ is open and classical, contrary to the calculated results. Furthermore, we show independently that the CNDO method has a built-in bias toward three-member ring formation by comparing the calculated total energy of propene *vs.* cyclopropane and allyl *vs.* cyclopropyl cation. In both cases the open chain form is thermodynamically far more stable than the three-membered ring isomer. Yet the calculated values (Table III) invariably favor the cyclic isomer! Since this behavior is followed whether one uses Wiberg's[4] or the original[3] parameters, it is clear that simple changes in parametrization are not responsible for these incorrect results. Since others[7] are "seeking to establish the limits of reliability of these [CNDO] calculations," the limitations manifested above must be noted.

Table III. Calculated Total Energies for C_3 Hydrocarbons and Cations

Compound	Total energy, au[a]
Propene[b]	−24.7513
Cyclopropane[b]	−24.8995
Allyl cation[c]	−23.4513
Cyclopropyl cation[d]	−23.5809

[a] Using Wiberg's parameters. [b] Structural parameters taken from L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958. [c] Assumed planar, C–C = 1.40, C–H = 1.08, all angles 120°. [d] The same structural parameters as were used for cyclopropane were utilized, except that the cationic center was assumed planar.

When the EHT method[8] is applied to the 2-phenylethyl system, entirely different results are obtained (Figure 1). The open form is energetically favored in both the cation (20 kcal mol^{-1}) and the radical (32 kcal mol^{-1}). That these results must also be quantitatively incorrect follows from the experimental observation that phenyl migration occurs[9] to a small but real extent in $PhCH_2CH_2\cdot$. Were this process to have an activation energy near 30 kcal mol^{-1} it would not compete with other experimental processes, and EHT is thus overestimating destabilization. It may also be that EHT may be biased *against* cyclopropane formation, since it predicts an open form for cyclopropanone,[10] whereas structural data[11] do not bear out this contention.

It is interesting to note that both CNDO/2 and EHT predict that the bridged radical, relative to the open species, is some 12–15 kcal mol^{-1} less stable than is the bridged cation, relative to the open cation. Insofar as this figure is valid, it permits one to estimate the relative stabilities of bridged *vs.* open cations by the following reasoning.

The neophyl radical is known to rearrange to its tertiary isomer,[12] both of which abstract hydrogen from aldehyde.

$$\mathrm{PhCMe_2CH_2\cdot} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{\cdot CMe_2CH_2Ph} \qquad (1)$$

$$\mathrm{PhCMe_2CH_2\cdot} + \mathrm{RCHO} \xrightarrow{k_2} \underset{\mathrm{P}}{\mathrm{PhCMe_2CH_3}} \qquad (2)$$

$$\mathrm{PhCH_2CMe_2\cdot} + \mathrm{RCHO} \xrightarrow{k_3} \underset{\mathrm{P'}}{\mathrm{PhCH_2CHMe_2}} \qquad (3)$$

Seubold[12] has claimed that the activation energy for hydrogen abstractions (2 and 3) and rearrangement (1) are the same. If one assumes that $k_2 \sim k_3$, and that $k_{-1} \ll k_2(\mathrm{RCHO})$, then the ratio of rearranged (P′) to unrearranged (P) hydrocarbon is

$$\frac{\mathrm{P'}}{\mathrm{P}} = \frac{k_1}{k_2(\mathrm{RCHO})}$$

From the Arrhenius equation, $k = Se^{-E/RT}$, it follows that the ratio S_1/S_2 can be evaluated from experimental data, since[12] $E_1 = E_2$. These data lead to $4 < S_1/S_2 < 8$. For the unsubstituted 2-phenylethyl radical

$$\mathrm{PhCH_2C^*H_2\cdot} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{\cdot CH_2CH^*{}_2Ph}$$

$$\mathrm{PhCH_2C^*H_2\cdot} + \mathrm{RH} \xrightarrow{k_2} \underset{\mathrm{P}}{\mathrm{PhCH_2C^*H_3}}$$

$$\mathrm{PhC^*H_2CH_2\cdot} + \mathrm{RH} \xrightarrow{k_2} \underset{\mathrm{P'}}{\mathrm{PhC^*H_2CH_3}}$$

$$\frac{\mathrm{P'}}{\mathrm{P}} = \frac{1}{1 + \dfrac{k_2}{k_1}(\mathrm{RH})} = \frac{1}{1 + (\mathrm{RH})\dfrac{S_2}{S_1}e^{-(E_2-E_1)/RT}}$$

From Slaugh's data for label rearrangement of 2-phenylethyl radical[13] (RH = 3-phenylpropionaldehyde), it is calculated that $E_1 = (E_2 + 4)$ kcal mol^{-1}. But E_2, the activation energy for hydrogen transfer, is thought[14] to be about 7 kcal mol^{-1}, which means $E_1 \sim 11$ kcal mol^{-1}. Identifying the activated complex for k_1 as the phenonium radical leads to the conclusion that the bridged radical is some 11 kcal mol^{-1} less stable than the open one.[15]

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(6) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969), and references cited therein.

(7) N. S. Isaacs, *Tetrahedron*, **25**, 3555 (1969).

(8) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(9) C. Walling, "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 427 ff.

(10) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(11) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *ibid.*, **91**, 1072 (1969).

(12) F. H. Seubold, *ibid.*, **75**, 2532 (1953).

(13) L. H. Slaugh, *ibid.*, **81**, 2262 (1959).

(14) Reference 9, p 429.

(15) This is a *maximum* estimate, since the activated complex may occur before symmetrical bridging.

If we now scale the CNDO and EHT curves additively so that the calculated potential energy surfaces reflect the energy difference between bridged and open radicals ($E\cdot = +11$ kcal mol^{-1} in Figure 1) and assume the cationic surface is similarly scaled, then one concludes that the bridged ion is 1–4 kcal mol^{-1} more stable than the open one.

In summary, neither CNDO or EHT MO calculations on the 2-phenethyl → phenonium cation give results which accord with experimental data. The deficiencies of CNDO for small ring compounds are quite serious, and its application to such problems must be approached with caution. Certainly the CNDO results quoted above must be viewed as merely suggestive and treated with reservation. For the time, at least, further information on this problem must await experimental results rather than those of calculation.

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Catalysis of Ionic Reactions by Polyelectrolytes. II. Electron Transfer between Cobalt(III) Complexes and Iron(II) in Solutions of Poly(vinylsulfonate)[1]

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Received June 4, 1970

Abstract: Dilute solutions of poly(vinylsulfonate) (PVS) accelerate by several orders of magnitude the reduction of $Co(NH_3)_5Cl^{2+}$, *cis*-$Co(NH_3)_4(N_3)_2^+$, and *trans*-$Co(NH_3)_4(N_3)_2^+$ by Fe^{2+}. The dependence of the reaction rate on polyion concentration, concentration of simple electrolyte, and reagent concentration is qualitatively similar to the characteristics of the previously reported polyanion-catalyzed reaction of $Co(NH_3)_5Cl^{2+}$ with Hg^{2+}. The reduction of $Co(NH_3)_4(N_3)_2^+$ is catalyzed by PVS much more powerfully with the trans isomer of the Co(III) complex, since this reaction is acid catalyzed and the complex ion bound to the polymer is in a region of high local hydrogen-ion concentration. A comparison of the PVS catalysis of $Co(NH_3)_5Cl^{2+}$ reactions with Hg^{2+} and Fe^{2+}, respectively, shows that the catalytic effect cannot be accounted for entirely by the concentration of the reagent ions in the polyion domain, but that this concentration also affects in some manner the activation process. On addition of PVS, the ΔE^* is reduced for the reaction with Hg^{2+} but increased for the reaction with Fe^{2+}.

In a previous communication from this laboratory,[2] it was demonstrated that small concentrations of polyanions may accelerate by very large factors reactions involving two cationic species. In particular, conditions were found where as little as 5×10^{-5} *N* poly(vinylsulfonate) (PVS) accelerated the Hg^{2+}-catalyzed aquation of $Co(NH_3)_5Cl^{2+}$ by a factor of 176,000.[3] It was proposed to interpret the dependence of the acceleration factor on the PVS concentration by two parameters, (a) the "effective local reagent ion concentration" in the polymer domain and (b) the product of the dissociation constants of the polyion with the two reagent ions. The second of these parameters could be evaluated by dialysis equilibrium, and the value thus obtained was in gratifying agreement with that estimated from kinetic data.

We are now extending this study to redox reactions involving Fe^{2+} as the electron donor and the species $Co(NH_3)_5Cl^{2+}$, *cis*-$Co(NH_3)_4(N_3)_2^+$, and *trans*-$Co(NH_3)_4(N_3)_2^+$ as electron acceptors.[4] In choosing these systems we had the following objectives. (1) The reactions of $Co(NH_3)_5Cl^{2+}$ with either Hg^{2+} or Fe^{2+} involve two species with a double positive charge, and it was of interest to determine whether both reactions are equally susceptible to polyanion catalysis. (2) In comparing the polyanion catalysis of the Fe^{2+} reduction of the cis and trans isomers of $Co(NH_3)_4(N_3)_2^+$, we hoped to find whether the affinity of a reagent species for the polyanion is sensitive to its dipole moment.

Results and Discussion

Reduction of Co(III) Complexes by Fe^{2+} in the Absence of Polyanions. Second-order rate constants for reactions of the three Co(III) complexes in the ab-

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* Address correspondence to this author.

(1) Abstracted from a Ph.D. thesis submitted by G. Gordimer to the Graduate School of the Polytechnic Institute of Brooklyn, June 1970. Financial support of this research by Research Grant No. GM 05811 of the National Institutes of Health is gratefully acknowledged.

(2) H. Morawetz and B. Vogel, *J. Amer. Chem. Soc.*, **91**, 563 (1969). This paper should also be consulted for a bibliography of related investigations.

(3) This effect is many orders of magnitude larger than the classical "kinetic salt effect" observed for reactions of ionic reagents in solutions of simple electrolytes. [See, *e.g.*, J. N. Brønsted and R. Livingston, *ibid.*, **49**, 435 (1927); A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949); G. Scatchard, *Nat. Bur. Stand.* (*U. S.*), *Circ.*, **500**, 185 (1953).] It should also be pointed out that the two effects are not superimposable. For instance, simple salts accelerate reactions of two cations in the absence of polyions but inhibit the catalysis of such reactions by polyanions.[2]

(4) The polyelectrolyte catalysis of redox reactions has recently been studied also by S. Brückner, V. Crescenzi, and F. Quadrifoglio, *J. Chem. Soc. A*, 1168 (1970), and by F. Quadrifoglio, V. Crescenzi, and A. Ius, *Proc. Symp. Coord. Chem., 3rd, 1970*, **1**, 73 (1970).