output reflectivities chosen were nearly optimum for energy output for the SeOCl₂-based system whereas it has not been established whether they are also optimum for POCl₃. Under these conditions thresholds occur in the region of 200 J (SeOCl₂ some 10% lower, POCl₃ 10% higher); however, with narrow-bore cells and higher reflectance output mirrors, both SeOCl₂- and POCl₃-based systems have shown thresholds as low as 10-J input.

Conclusions

On the basis of these experiments, it is clear that the differences between the two liquid laser systems are not large. The POCl₃ system starts with the advantages of lower corrosiveness and toxicity and under one set of experimental conditions shows a higher slope efficiency of power output. Nevertheless, its over-all decay time of fluorescence is lower (some 20% below what is calculated from spectroscopic considerations), and therefore it presumably has a lower quantum efficiency than has the SeOCl₂ system. On the whole, however, both systems are quite similar in their physical characteristics and the choice of one or the other would be dictated largely by experimental conditions.

The Balance of Steric and Conjugative Effects in Phenyl-Substituted

Cations, Radicals, and Anions

by Roald Hoffmann, Robert Bissell, and Donald G. Farnum

Department of Chemistry, Cornell University, Ithaca, New York 14850   (*Received December 9, 1968*)

The delicate balance of steric and conjugative effects which determines the equilibrium geometry of phenyl-substituted carbonium, allyl, pentadienyl, cyclopropenyl, cyclopentadienyl, and cycloheptatrienyl cations, radicals, and anions is studied by means of extended Hückel calculations. Despite some doubts as to the applicability of this method to such species, the resulting potential energy curves are reasonable. In triphenyl-carbonium ion there is found no evidence for a local minimum other than that in the propeller geometry. In di-phenylcarbonium ion the transition from the equilibrium geometry to its enantiomer is most easily accomplished through a transition state in which one phenyl group is coplanar, the other perpendicular. In the triphenyl-carbonium ion the corresponding conversion is estimated to proceed through a transition state in which all phenyl rings are perpendicular. In all cases the anions are predicted to be conformationally more stable than the cations. Hyperconjugative charge transfer occurs to *ortho* carbons of a phenyl ring as it is twisted out of conjugation. The potential energy curve for twisting the phenylcyclopropenium cation out of planarity is calculated to be very flat. This insensitivity of energy to rotation is not matched by absence of charge transfer. Several theoretical explanations for the calculated insensitivity of phenylcyclopropenium energy to twist of phenyl group are discussed, but none is completely satisfactory.

Introduction

Phenyl groups may stabilize carbonium ions, radicals, and carbanions. This stabilization is a consequence of delocalization and is achieved through a π-type interaction. The maximum effect will be obtained when the phenyl group is coplanar with the adjacent ion or radical center, assumed trigonal. When several phenyl groups are attached, an all-planar geometry often is made impossible by short H–H contacts. The equilibrium conformations of these molecules are then determined by a delicate balance of steric and conjugative effects. It is this balance that we explore in this paper for phenyl- (PhCH₂), diphenyl- (Ph₂CH), and triphenyl- (Ph₃C) carbonium ions, radicals, and anions, phenyl-

(PhC₃H₂⁺), diphenyl- (Ph₂C₃H⁺), and triphenyl-(Ph₃C₃⁺) cyclopropenium cations, phenylcyclopenta-dienide anion (PhC₅H₄⁻), phenyltropylium ion (PhC₇H₆⁺), and phenylallyl (PhC₃H₄) and phenylpentadienyl (PhC₅H₆) species.

Arylcarbonium Ions, Radicals, and Carbanions

That planar conformations of Ph₂CH and Ph₃C are sterically impossible was apparent to some early workers in the field. The first clear suggestion of rotated geometries seems to be due to Lewis and coworkers[1] and to Seel.[2]

(1) G. N. Lewis, T. M. Magel, and D. Lipkin, *J. Amer. Chem. Soc.*, **64**, 1774 (1942).

Lewis, Magel, and Lipkin[1] examined the electronic spectrum of crystal violet and suggested the presence of two distinct conformations of the tri-p-(dimethylamino)phenylcarbonium ion. The first of these was the propeller geometry I in which each phenyl group was twisted by some angle θ from the plane defined by the four central carbons. I has D_3 symmetry. The second conformation suggested was the inverted form II, unsymmetric, in which one of the three rings was twisted in an opposite sense to the other two.

I   II
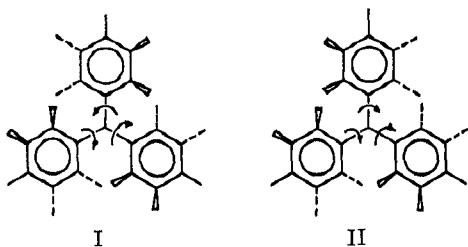
Subsequently the interpretation of Lewis regarding the spectral evidence for conformation II was challenged,[3] but the original suggestion of the two geometries I and II has had considerable impact on further work in this area. Seel[2] in a controversy with W. Theilacker independently suggested the propeller geometry for the Ph_3C radical and calculated on the basis of van der Waals radii that the angle of twist θ had to be greater than 20°. Similar calculations by Szwarc[4] led to a θ of approximately 30°. Interest in the radical was revived when its electron spin resonance spectrum was observed. The spectrum was interpreted in terms of a twisting of approximately 30° by Adam and Weissman.[5] The related dimesitylmethyl radical gave an esr spectrum interpretable on the basis of further twisting.[6] A thorough investigation into the potential surface of diphenylmethyl was carried out by Adam and Falle,[7] who concentrated on the interconversion of enantiomeric Ph_2CH geometries. There has also appeared recently a promising endor study of a radical closely related to Ph_3C, in which an activation energy to interconversion of enantiomeric propeller geometries has been measured.[8] Triphenylmethyl radical has been investigated by electron diffraction in the vapor phase,[9] and a twist angle of approximately 45° has been assigned to the molecule. The same group carried out a crystallographic investigation of tri-p-nitrophenylmethyl radical[10] and found angles of twist of 40, 30, and 30° for the phenyl rings.

In the carbonium ion case some initial indications for type II geometry[11] were superceded by more convincing arguments for the propeller shape I.[12] Deno and co-workers[13] also estimated from van der Waals radii that a twist angle of ~25° was minimal for the arylcarbonium ions. Nuclear magnetic resonance studies formed the next contributions to the field.[14,15] To obtain agreement with measured chemical shifts an angle of twist of ~23°[14] or ~30°[15] was required. Fluorine nmr

studies of *meta*-substituted triphenylcarbonium ions[16] have yielded for a combination of ring-flipping motions the activation parameters $\Delta H^{\ddagger} = 9$ kcal/mol, $\Delta S^{\ddagger} = -17$ eu at $-43.3°$. The motion in which three rings flip synchronously proceeds considerably faster than one- or two-ring flips. A thorough single-crystal X-ray structure has appeared of a salt of Ph_3C^+. In the crystal the D_3 propeller geometry is found[17] with a twist angle of 31.8 $\pm$ 0.6°. A somewhat less informative crystal structure of tri-p-methoxyphenylcarbonium ion[18] is consistent with a maximum twist of phenyl groups of 30°. In the case of tri-p-aminophenylcarbonium perchlorate, the crystal structure[19] reveals a propeller-shaped cation with angles of twist of 27, 34, and 34°.

The $PhCH_2$, Ph_2CH, and Ph_3C carbanions have received sparing attention. An nmr study has been reported by Sandel and Freedman.[20] It yields no information on the twist angle (or on the planarity at the central carbon) but there appear significant differences between the anion and cation spectra.

We also wish to mention a detailed study of triarylboranes, Ar_3B, by Weismann and Schug.[21] The boranes are isoelectronic with the corresponding carbonium ions. Potential energy curves for twisting in a propeller geometry were calculated in this work by considering the total energy as a sum of two factors—

(2) F. Seel, *Naturwissenschaften*, **31**, 504 (1943).

(3) C. W. Looney and W. T. Simpson, *J. Amer. Chem. Soc.*, **76**, 6293 (1954).

(4) M. Szwarc, *Discussions Faraday Soc.*, **2**, 39 (1947).

(5) F. C. Adam and S. I. Weissman, *J. Amer. Chem. Soc.*, **80**, 2057 (1958).

(6) Estimated as 60–70° by A. D. MacLachlan, *J. Chem. Phys.*, **32**, 1488 (1960), and revised to 50–60° by D. B. Chesnut and G. J. Sloan, *ibid.*, **35**, 443 (1961). See also D. R. Dalton, S. A. Liebman, H. Waldman, and R. S. Sheinson, *Tetrahedron Lett.*, 145 (1968).

(7) F. C. Adam and H. R. Falle, *Can. J. Chem.*, **44**, 1387 (1966).

(8) J. S. Hyde, R. Breslow, and C. DeBoer, *J. Amer. Chem. Soc.*, **88**, 4763 (1966).

(9) P. Andersen, *Acta Chem. Scand.*, **19**, 629 (1965).

(10) P. Andersen and B. Klewe, *ibid.*, **21**, 2599 (1967).

(11) M. S. Newman and N. C. Deno, *J. Amer. Chem. Soc.*, **73**, 3644 (1951); G. Branch and H. Walba, *ibid.*, **76**, 1564 (1954).

(12) D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.*, 675 (1957).

(13) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954); N. C. Deno, P. T. Groves, and G. Saines, *J. Amer. Chem. Soc.*, **81**, 5790 (1959).

(14) D. E. O'Reilly and H. P. Leftin, *J. Phys. Chem.*, **64**, 1555 (1960).

(15) R. S. Berry, R. Dehl, and W. R. Vaughan, *J. Chem. Phys.*, **34**, 1460 (1961).

(16) A. K. Colter, I. I. Schuster, and R. J. Kurland, *J. Amer. Chem. Soc.*, **87**, 2279 (1965); I. I. Schuster, A. K. Colter, and R. J. Kurland, *ibid.*, **90**, 4679 (1968).

(17) A. H. Gomes de Mesquita, C. H. MacGillavry, and K. Eriks, *Acta Cryst.*, **18**, 437 (1965).

(18) P. Andersen and B. Klewe, *Acta Chem. Scand.*, **10**, 791 (1965).

(19) L. L. Koh, *Dissertation Abstr.*, 3860 (1965).

(20) V. R. Sandel and H. H. Freedman, *J. Amer. Chem. Soc.*, **85**, 2328 (1963).

(21) T. J. Weismann and J. C. Schug, *J. Chem. Phys.*, **40**, 956 (1964).

nonbonded interactions and a π-electronic energy. Twist angles of around 43° were obtained for the most symmetrical configurations. "Inverted" forms (one unsymmetrical aryl group twisted 180° from the C_3 geometry) were also calculated. Agreement with geometries extrapolated from observed nmr shifts was not good.

Calculations

In our theoretical analysis we have used extended Hückel calculations.[22] There are some theoretical reasons why these should not be reliable for calculations on ions.[23] We preferred a pragmatic approach and proceeded to investigate if reasonable potential energy curves were emerging. The reader will shortly see that such were. Idealized distances were: C–C aromatic, 1.40 Å; C–H, 1.10 Å; C–C$^+$, 1.50 Å; 120° angles everywhere. We have not examined nontrigonal conformations, and this may be a source of error in the case of the carbanions.

For benzyl only one degree of freedom (III) was studied, namely, the rotation of the terminal methylene group. An extensive search of the benzhydryl potential surfaces included not only the favored conrotatory motion[24] (IV) but also all possible simultaneous

III   IV
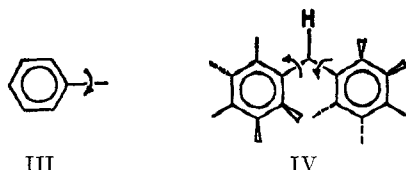
rotations of the two phenyl groups. The trityl calculations are still time consuming and therefore expensive, and so we limited ourselves to the D_3 and C_1 geometries (I and II) previously discussed.

Figures 1, 2, and 3 present the calculated potential curves for motions III, IV, and I of the cations and anions. The radical curves will be precisely intermediate between the two. As anticipated benzyl cation and anion prefer a planar equilibrium geometry while the other molecules compromise at an intermediate rotation angle. The functional form of the energy variation of $PhCH_2{}^+$ is very close to $\cos^2 \theta$. It is most interesting that we calculate benzyl anion to be conformationally more stable than the cation. We have noted a similar conclusion for the allyl system elsewhere[25] and will return to a discussion of this phenomenon below. For diphenyl- and triphenylcarbonium this trend is reinforced; i.e., the anion minima are deeper and correspondingly the equilibrium angle smaller than for the cation. The calculated equilibrium angles ($\pm 2°$) are

Ph_2CH^+	Ph_2CH^-	Ph_3C^+	Ph_3C^-
36°	31°	44°	35°

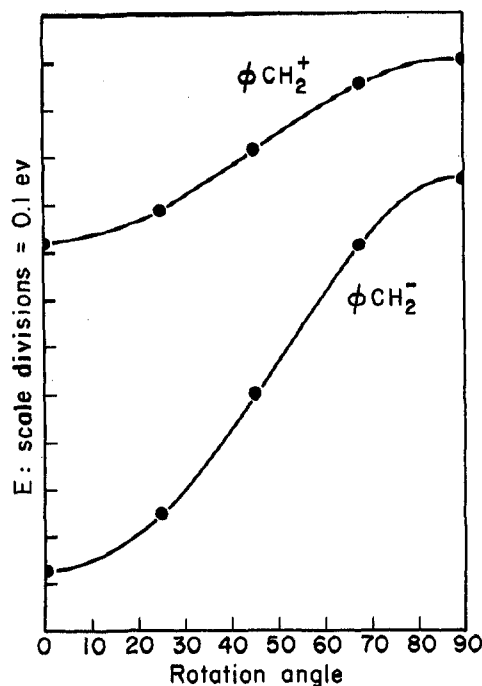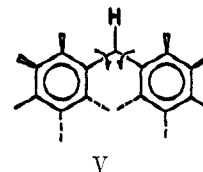For the diphenylmethyl system we have varied both rotational degrees of freedom simultaneously. The

Figure 1. Potential energy vs. angle of twist for benzyl cation and anion.

exploration of disrotatory motions (V) showed these to

V

be consistently at higher energy than the conrotatory modes. The results for the latter are presented in the form of a contour diagram (Figure 4), in which the axes measure the angles of rotation of phenyl groups 1 and 2 away from coplanarity with the carbonium hydrogen. Along the line $\alpha = \beta$ the molecule is characterized by a twofold symmetry axis passing through the carbonium C–H bond, but away from that line the molecules lack any symmetry.

The contour diagram clearly shows that the equilibrium geometry is one with a twofold axis of symmetry; i.e., $\alpha = \beta$, rather than some compromise with one phenyl ring planar and the other twisted. The pathways of interconversion of one equilibrium geometry into its enantiomer have been discussed in some detail by Adam and Falle.[7] Three possible geared motions

(22) R. Hoffmann, J. Chem. Phys., **39**, 1397 (1963); **40**, 2474, 2480, 2745 (1963); Tetrahedron, **22**, 521, 539 (1966); and subsequent papers. We used a Slater exponent for H of 1.3, and other parameters were maintained at values used in the above references.

(23) C. A. Coulson and M. J. S. Dewar, Discussions Faraday Soc., **2**, 54 (1947).

(24) Possessing C_2 symmetry; defined in R. B. Woodward and R. Hoffmann, J. Amer. Chem. Soc., **87**, 395 (1965).

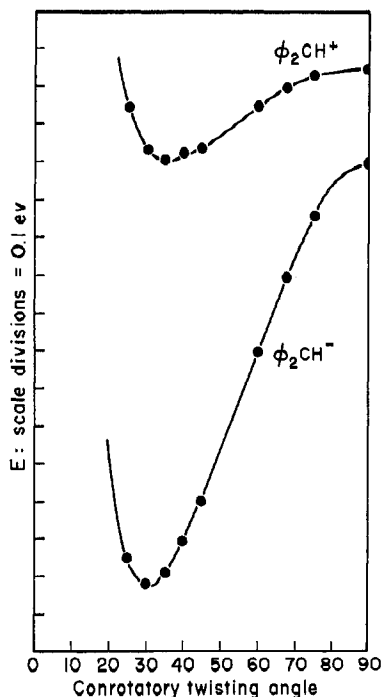(25) R. Hoffmann and R. A. Olofson, ibid., **88**, 943 (1966).

Figure 2. Potential energy vs. angle of twist of each phenyl group for diphenylcarbonium ion and carbanion.

are shown schematically below. In VI the transition state is planar ($\alpha = 0°$, $\beta = 0°$); in VII it has both phenyl groups perpendicular to the plane of the central carbon and its ligand atoms ($\alpha = 90°$, $\beta = 90°$); and in VIII one phenyl ring is coplanar, the other perpendicular ($\alpha = 90°$, $\beta = 0°$).
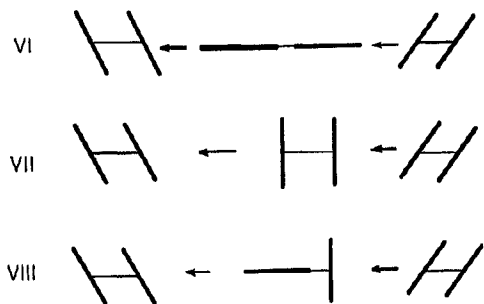

Figure 4 clearly shows that the transition state for motion VI is the worst, while that for VIII is clearly the easiest. The barrier for a geared motion such as VIII is essentially negligible, as was pointed out by Adam and Falle.[7] Recent observations of the nmr spectra of dimesitylcarbonium ions[26] also indicate a small barrier to internal rotation and suggest a geared motion of type VIII.

The greater conformational stability of anions over cations is in the extended Hückel method a direct consequence of the behavior of the nonbonding molecular orbital. The angular dependence of the energy of this MO is plotted in Figure 5 for $PhCH_2$, Ph_2CH, and Ph_3C. In each case this orbital is destabilized as one rotates from the planar geometry. Thus placing electrons
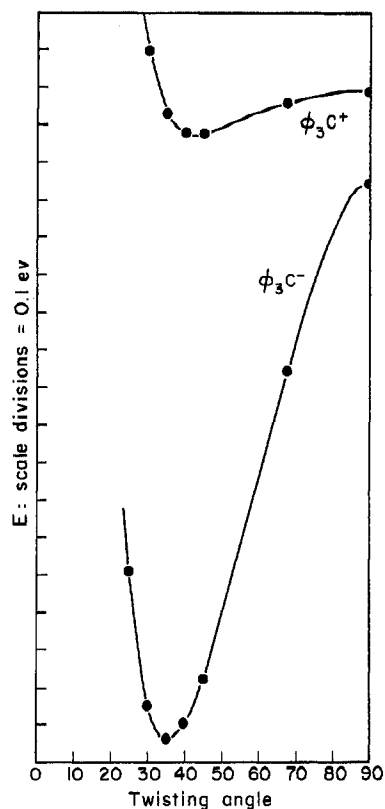
Figure 3. Potential energy vs. angle of twist of each phenyl group, in a propeller geometry, for triphenylcarbonium ion and carbanion.
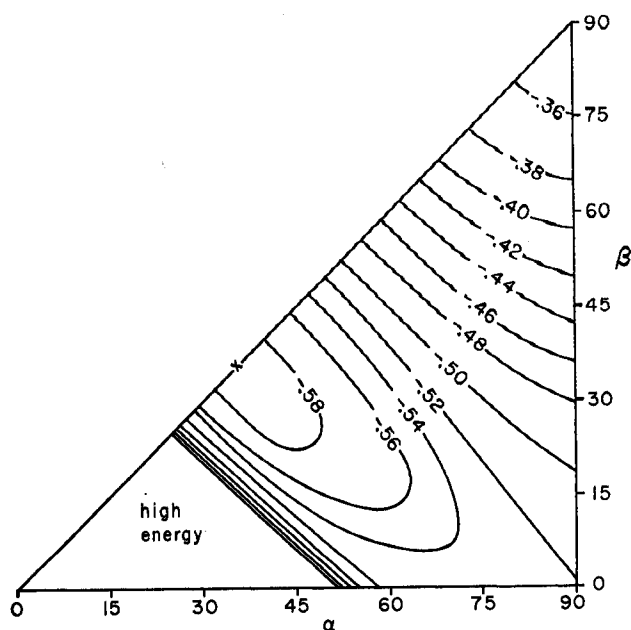

Figure 4. Energy surface for independent twisting of one phenyl group (α) and the other phenyl group (β) in diphenylcarbonium. The energy contours are in electron volts relative to an arbitrary energy zero.

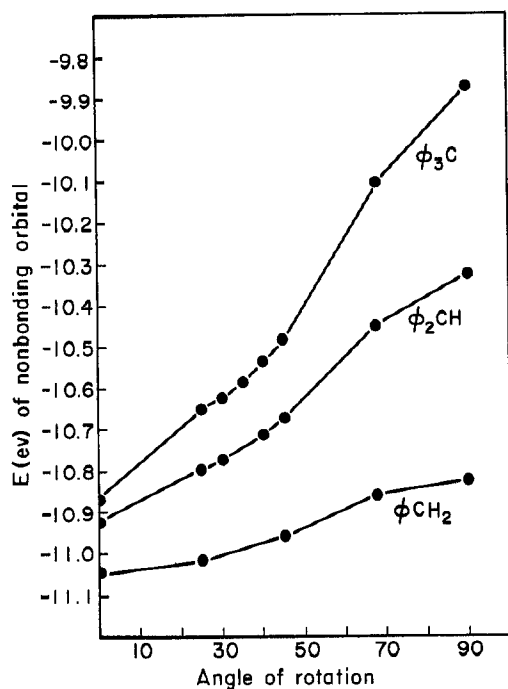(26) H. Kwart and S. Alekman, J. Amer. Chem. Soc., 90, 4482 (1968).

Figure 5. Energy of nonbonding molecular orbital as a function of angle of twist for $PhCH_2$, Ph_2CH, and Ph_3C.
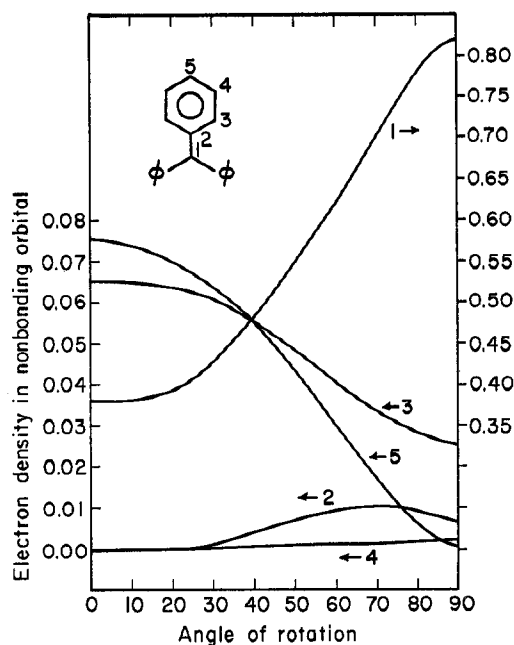

Figure 6. Electron density of a single electron in the nonbonding orbital of Ph_3C as a function of twist angle in the propeller conformation. Note that the electron density at position 1 refers to the right-hand scale, whereas the other positions are measured on the left-hand scale, which is an expanded one.

evident in Figure 6, which shows the distribution $(\sigma + \pi)$ of a single electron in the nonbonding MO of Ph_3C as a function of rotation. The corresponding curves for Ph_2CH and $PhCH_2$ are very similar, except that delocalization in the planar geometry is less extensive. We do not, however, believe that the increase in energy of the nonbonding MO with increasing twist angle is due to a stabilization of this orbital in the planar geometry as a consequence of delocalization. Notice that in Figure 5 the three species studied have their nonbonding MO's at nearly the same energy at $\theta = 0°$ but differing widely at $\theta = 90°$. This implies to us that the nonbonding MO is rather being destabilized as twisting increases. A possible source of this destabilization could be a stronger interaction of the nonbonding MO with the σ rather than the σ^* levels of the phenyl group. We have consistently found this type of hyperconjugative interaction to be destabilizing for a nonbonding molecular orbital.

There is little experimental information regarding the conformational stability of benzyl cations and anions. Direct observation of substituted benzyl cations in SbF_5–SO_2 solution has been achieved,[27] and no evidence of rotation was apparent at temperatures below 0°.

We examined briefly the question of the possible existence of a second local minimum for Ph_3C^+, corresponding to geometry II, sometimes called a "skew-helix." We held two phenyl rings in the equilibrium propeller geometry at an angle of twist of 45° and varied the twist angle of the third phenyl ring. The results are displayed in Figure 7. There is a large region of angles of twist of the third phenyl ring, between 30 and 90°, in which the energy varies little. There is no indication of a second minimum of a "skew–helix"

in this orbital on going from cation to radical to anion would tend to increase the resistance to rotation and thus deepen the anion minima.

An electron in the nonbonding molecular orbital is clearly least localized in a planar geometry. This is
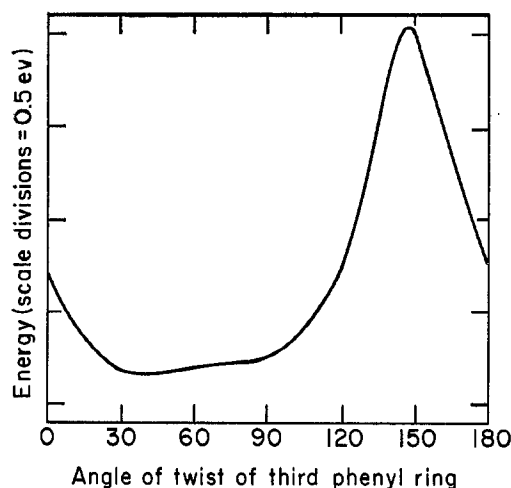

Figure 7. The potential energy of a Ph_3C^+ in which two rings are fixed at a 45° angle from planarity and the orientation of the third ring is varied.

(27) J. M. Bollinger, M. B. Comisarow, C. A. Cupas, and G. A. Olah, J. Amer. Chem. Soc., 89, 5687 (1967).

or "inverted" type. It must be kept in mind, however, that we did not allow the first two rings the freedom to move, and a slight probability of a second minimum remains until this constraint is relaxed.

Schuster, Colter, and Kurland, in their productive and careful study of the nmr spectra of fluorine-substituted triphenylcarbonium species,[16] interpreted the observed preference for a three-ring flip in terms of the following interconversion scheme. Our calculations

Scheme I
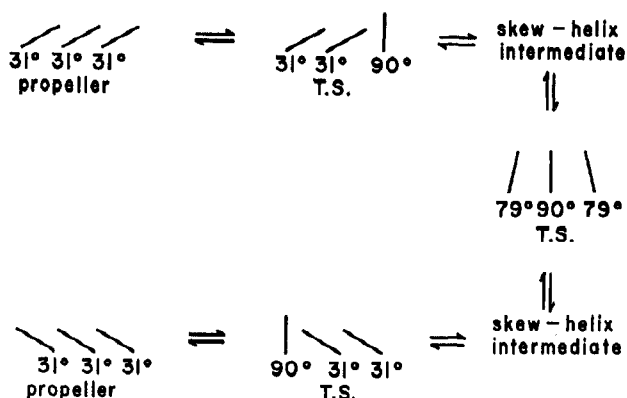
differ from this scheme in one important way, namely, in not predicting an energy minimum for the "skew–helix" conformation. Though we have not specifically calculated the 79°–90°–79° transition state postulated by these workers, we believe that it cannot differ in any significant way in energy from a 90°–90°–90° transition state, a formally nonconjugated system. It seems likely to us that the energy difference between these two conformations must be small, not only in our calculations but also in the Hückel approximation used by Kurland, et al. It must be emphasized that we are not attributing any superiority to our semiempirical method; the difference between the equilibrium geometry and the 90°–90°–90° conformation is only 2.8 kcal/mol in our calculation (Figure 3). The depth of the well will be very sensitive to the extent to which our calculations properly gauge the steric interaction; it is clear that the calculated barrier is only some 30% of the observed value.

Because the nuclear magnetic resonance spectra of the carbonium ions have been extensively studied, it was also of interest to calculate the charge distribution as a function of rotation in these molecules. There are two possible quantities which could be displayed here. The better defined one is the total charge on the carbons, $\sigma + \pi$. The π component is very difficult to isolate for nonplanar Ph_2CH^+ and Ph_3C^+ since what is π for one ring is partially σ for the other. So we have illustrated in Figures 8, 9, and 10 the π and $\sigma + \pi$ charge distributions for benzyl cation, but only $\sigma + \pi$ for Ph_3C^+.

There are several interesting features of these charge distributions. The electron density at ortho and para positions increases rapidly with rotation. In the π-

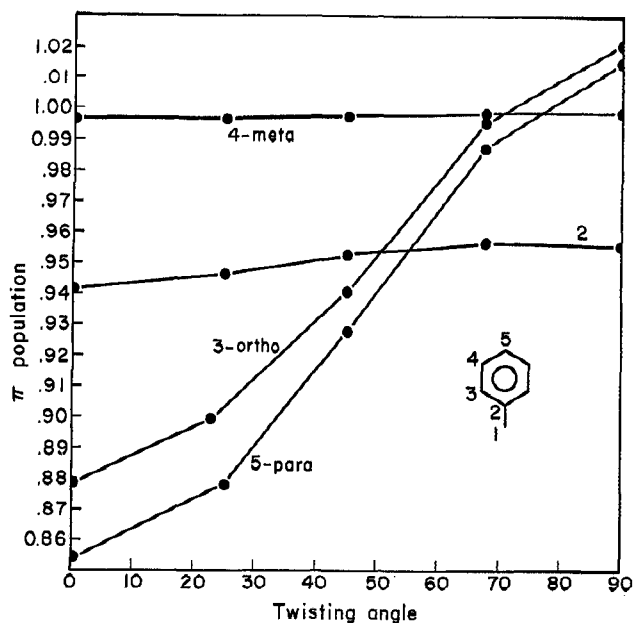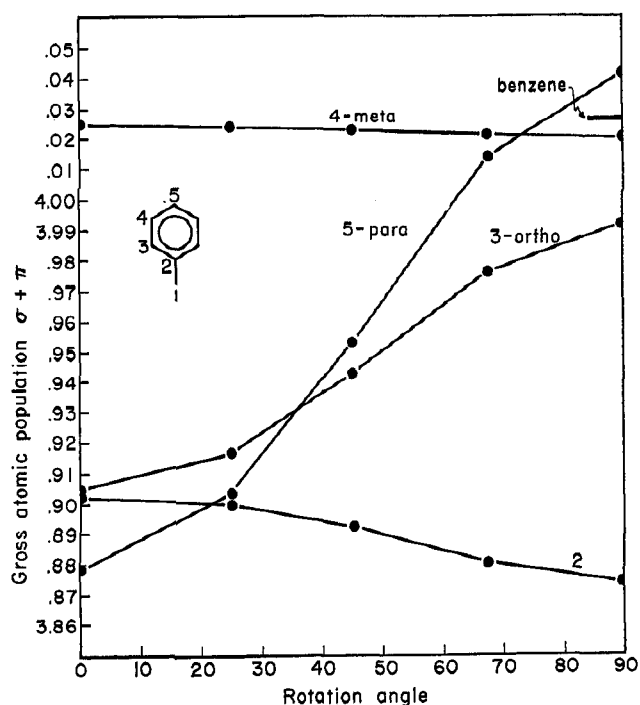Figure 8. π-Electron density in benzyl cation as a function of twisting.

Figure 9. Total $\sigma + \pi$ electron density in benzyl cation as a function of twisting.

electron density the two curves run parallel, with para more positive than ortho. When the total $\sigma + \pi$ density is formed, the para curve is unaffected, the already flat meta curve changed little, but the ortho position becomes definitely more positive, so that the ortho- and para-electron densities cross near 35°. This behavior is the result of a hyperconjugative charge transfer from the carbonium ion site to the phenyl σ
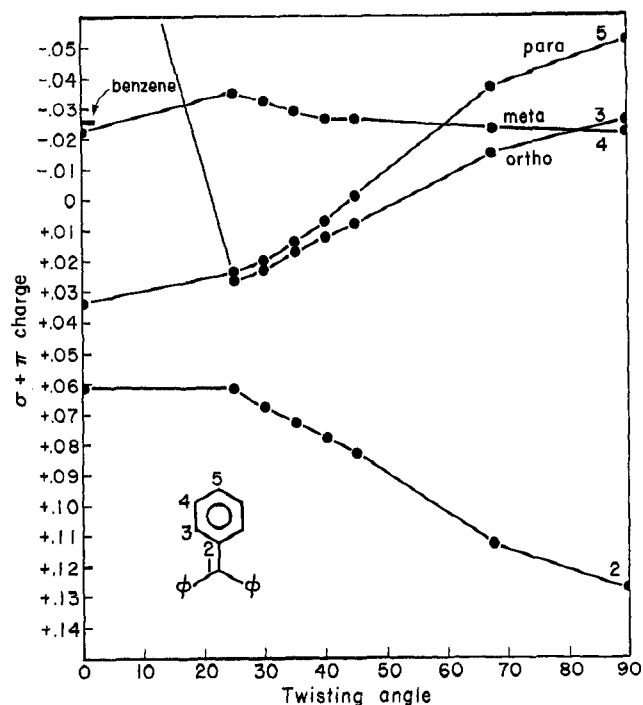
Figure 10. Total $\sigma + \pi$ electron density in triphenylcarbonium ion as a function of propeller twisting.

bonds, with the maximum effect at $\theta = 90°$. This effect is small at the 2 position, maximal at the *ortho* carbons, and very rapidly attenuated at further carbons.

In Ph_3C^+ the *ortho* hydrogens are sterically very unhappy near the planar geometry. As a result electrons are pushed off the sterically crowded hydrogens, and the hydrogens become quite positive—a general effect we have noted elsewhere as well. The electrons are displaced from the hydrogens to the nearest carbons, and this is responsible for the large negative charge increment on *ortho* carbons near the planar configuration. In Ph_2CH^+ (charges not shown) there are two nonequivalent *ortho* and *meta* positions. The crowded *ortho* position behaves as the corresponding site in Ph_3C^+ but the other *ortho* position remains normal. The calculated charge densities at ring carbons are in poor agreement with the charges extrapolated from the nmr studies,[28,29] with the consolation that other computations have not done much better.

The decomposition of the charge transfer in phenyl-carbonium ions is most interesting. Consider benzyl cation. At $\theta = 0°$ the phenyl ring is 0.286 of an electronic charge more positive than at $\theta = 90°$. Of this charge transfer 0.270 is derived from the p orbital of the carbonium ion. The π system of the phenyl is 0.466 of an electronic charge more positive at $\theta = 0°$ than at $\theta = 90°$. This π-charge transfer is balanced by a reverse charge transfer of no less than 0.168 of an electron from the σ system of phenyl to the carbonium ion p; *i.e.*, the σ system of the phenyl group is by that amount more positive at $\theta = 90°$ than at $\theta = 0°$. This

reverse charge transfer, the result of hyperconjugation, is thus more than one-third of the classical charge transfer.

Arylcyclopropenium and Other Aromatic Ions

Triphenylcyclopropenium cation ($Ph_3C_3^+$, IX) was synthesized in 1957.[30,31] Because the assumption of

IX
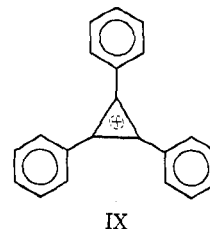
reasonable C–C distances and angles put the nearest H–H distances at approximately the van der Waals contact of 2.4 Å, all subsequent molecular orbital calculations or discussions of the geometry of this species or of the phenylcyclopropenium ($PhC_3H_2^+$) or diphenyl-cyclopropenium ($Ph_2C_3H^+$) cations were reasonably based on a strictly planar molecular geometry.[32-37]

The first suggestion of noncoplanarity of the rings in $Ph_3C_3^+$ was made in connection with a study of the paramagnetic resonance spectrum of a triplet state of $Ph_3C_3^+$ perchlorate and bromide.[38] The rotation out-of-plane was believed to be slight. An X-ray diffraction study[39] of the perchlorate salt indicates a slight noncoplanarity of the phenyl rings. The three rings are twisted in a conrotatory or propeller manner, making angles of 7.6, 12.1, and 21.2° with respect to the C_3 plane.

Our study of the arylcyclopropenium species was based on the geometry derived in the crystallographic study. We assumed C–C distances in the three-membered ring of 1.37 Å, ring-phenyl bond 1.45 Å, idealized hexagonal phenyl groups with C–C 1.40 Å. The 99-orbital $Ph_3C_3^+$ is the largest molecule we have yet calculated in an extended Hückel computation. Figure 11 shows the calculated potential energy curve

(28) D. G. Farnum, *J. Amer. Chem. Soc.*, **89**, 2970 (1967); G. Fraenkel and D. G. Farnum in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer Ed., John Wiley & Sons, Inc., New York, N. Y., 1968, p 237.

(29) G. J. Ray, A. K. Colter, D. G. Davis, D. E. Wisnosky, and R. J. Kurland, *Chem. Commun.*, 815 (1968).

(30) R. Breslow, *J. Amer. Chem. Soc.*, **79**, 5318 (1957); R. Breslow and C. Yuan, *ibid.*, **80**, 5991 (1958).

(31) Reviewed by A. W. Krebs, *Angew. Chem.*, **77**, 10 (1965).

(32) D. A. Bochvar, I. V. Stankevich, and A. L. Chistyakov, *Zh. Fiz. Khim.*, **33**, 2712 (1959); **34**, 2543 (1960).

(33) S. L. Manatt and J. D. Roberts, *J. Org. Chem.*, **24**, 1337 (1959).

(34) R. Basu and S. K. Bose, *Theoret. Chim. Acta*, **4**, 94 (1966).

(35) R. Breslow, J. Lockhart, and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2375 (1961).

(36) R. Breslow and H. W. Chang, *ibid.*, **83**, 2367 (1961).

(37) R. Breslow, W. Bahary, and W. Reinmuth, *ibid.*, **83**, 1763 (1961).

(38) M. S. de Groot, I. A. M. Hesselman, and J. H. Van der Waals, *Mol. Phys.*, **10**, 241 (1966).

(39) M. Sundaralingam and L. H. Jensen, *J. Amer. Chem. Soc.*, **88**, 198 (1966).
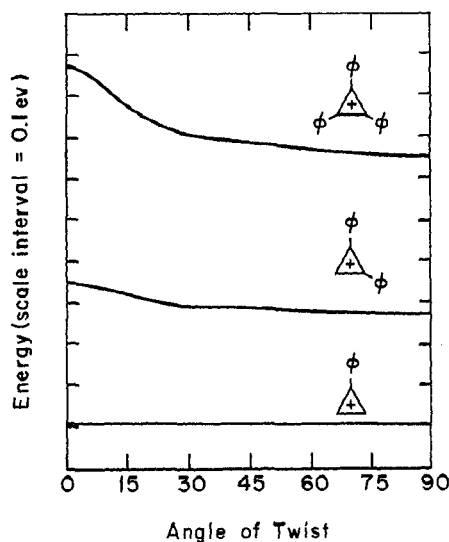
Figure 11. Calculated potential energy curves for twisting of phenylcyclopropenium cations.

Table I: Charges on Phenyl Rings in Planar and Perpendicular Conformations[a]

Molecule	$Q(\theta = 0°)$	$Q(\theta = 90°)$	Charge delocalized[b]
$PhCH_2^+$	+0.484	+0.198	0.286
Ph_2CH^+	+0.300	+0.143	0.157
Ph_3C^+	+0.219	+0.110	0.109
$PhC_3H_2^+$	+0.139	+0.049	0.090
$Ph_2C_3H^+$	+0.131	+0.044	0.087
$PhC_5H_4^-$	−0.064	−0.013	0.051
$PhC_7H_6^+$	+0.060	+0.016	0.044
$2\text{-}PhC_3H_4^+$	+0.028	+0.021	0.007
$1\text{-}PhC_3H_4^+\text{-}trans$	+0.282	+0.107	0.175
$1\text{-}PhC_3H_4^+\text{-}cis$	+0.277	+0.107	0.170
$1\text{-}PhC_5H_6^+\text{-}trans$	+0.209	+0.085	0.124

[a] The table lists charges Q on each C_6H_5 unit when more than one phenyl ring is present. In such cases the $\theta = 90°$ geometry is that with all phenyl rings at 90°; the $\theta = 0°$ geometry one with all phenyl rings at 0°. [b] $Q(\theta = 0°) - Q(\theta = 90°)$ for cations and the negative of this difference for anions. This is the electron density delocalized from Ph to cation center or from the anion center to Ph.

for simultaneous twisting of all rings in $Ph_3C_3^+$. The computations yield a shallow minimum for all rings perpendicular to the C_3 plane. This is in disagreement with the extrapolation of the crystallographic study and with common conceptions of the geometry of this molecule. However, the difference in energy between a coplanar and perpendicular form is only 0.23 eV, some 5.3 kcal. Figure 11 also shows the calculated potential energy curves for $Ph_2C_3H^+$ and $PhC_3H_2^+$. These are increasingly flatter, with the phenylcyclopropenium curve being indistinguishable from horizontal on the scale of the figure. The actual energy difference between 0 and 90° that is calculated for this molecule is 0.0017 eV and is at the level of accumulated round-off errors in the calculation.

In our calculations phenylcyclopropenium cation is thus energetically indifferent to the torsional angle. This does not imply that the charge transfer to the phenyl group is invariant to phenyl rotation. Table I lists the charges per C_6H_5 unit for planar and perpendicular geometries of the molecules we have studied. It is seen that in $PhC_3H_2^+$ the phenyl ring is by 0.090 of an electronic charge more positive at $\theta = 0°$ than at $\theta = 90°$. Examination of intermediate angles reveals a nearly perfect $\cos^2 \theta$ angular dependence of the charge transfer; thus charge is delocalized, but the effect on the energy is negligible for phenylcyclopropenyl. If true, this could be interpreted in two related ways: (1) to gain energetically from delocalization one must place the phenyl group at a site where in the absence of a planar phenyl group a great amount of positive charge would be localized; (2) an aromatic set of electrons, $4q + 2$ in number, can gain little energetically from further delocalization. To probe these points we carried out calculations on phenylcyclopentadienide anion, phenyltropylium cation, 2-phenylallyl cation, cis- and trans-1-

phenylallyl cations, and trans-1-phenylpentadienyl cation. The potential energy curves for these molecules are shown in Figures 12 and 13 and the extent of charge delocalization may be obtained from Table I.

Phenylcyclopentadienide anion has a very shallow minimum near $\theta = 20°$, with the slight maximum at $\theta = 0°$ probably hinting of the beginning of a steric problem in the planar geometry. Elsewhere we have exhibited the extended Hückel potential surface for biphenyl,[40] in which the planar conformation is disfavored and a compromise struck at $\theta \simeq 45°$. Consistent with this progression from five- to six- to seven-membered ring and the attendant deterioration of the steric situation in the coplanar geometry is the computed potential energy surface for phenyltropylium. A minimum is found near $\theta = 60°$, with only a low barrier at $\theta = 90°$. Thus both phenylcyclopentadienide and phenyltropylium, in exhibiting intermediate minima, indicate some energetic advantage for the coplanar geometry. In these species, moreover, less charge is transferred to the phenyl group than in phenylcyclopropenyl, so the latter remains an anomaly. The extent of non-planarity of phenyltropylium has been briefly discussed in connection with a study of the uv spectra of some substituted derivatives.[41] There has been one estimate of 25–29° twist in pyridiniumcyclopentadienides.[42]

The phenylallyl cation potential energy curves appear entirely reasonable and reinforce our belief in the faithfulness of the model. $1\text{-}PhC_3H_4^+\text{-}trans$ has the least steric problem in a planar geometry, with only one

(40) A. Imamura and R. Hoffmann, J. Amer. Chem. Soc., 90, 5379 (1968).

(41) C. Jutz and F. Voithenleitner, Chem. Ber., 97, 29 (1964).

(42) J. A. Berson, E. M. Evleth. Jr., and S. L. Manatt, J. Amer. Chem. Soc., 87, 2901 (1965).
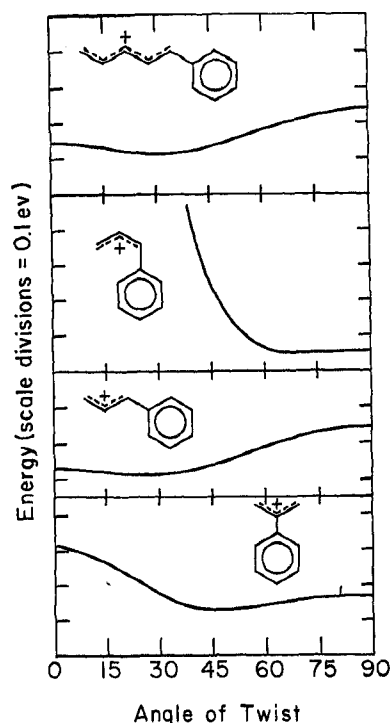
Figure 12. Calculated potential energy curves for some phenylallyl and phenylpentadienyl cations.
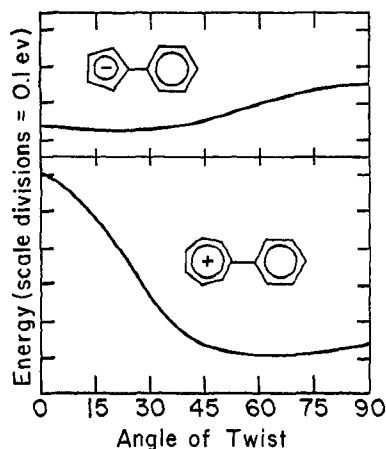

Figure 13. Calculated potential energy curves for phenylcyclopentadienide anion and phenyltropylium cation.

reasonably small H–H contact at a distance comparable to the *ortho–ortho'* interaction in biphenyl. This is reflected in the very low barrier to a planar conformation. 2-PhC$_3$H$_4$$^+$ creates H–H contacts nearly identical with those in biphenyl, and the potential energy curve is accordingly similar. 1-PhC$_3$H$_4$$^+$-*cis* would have an extremely short H–H distance of 0.66 Å in a planar geometry, and this is reflected in the steeply rising energy at small angles of twist. The very small charge delocalization calculated for 2-phenylallyl cation compared to the sizable effect on 1-phenyl substitution is readily understandable. The low-lying, nonbonding allyl orbital, which would stabilize the phenyl group

by interacting with appropriate symmetry orbitals in it has a node at the central carbon of the allyl chain, and so substitution there is ineffective. Or, in other language, the positive charge in an allyl cation resides predominantly on the terminal carbons, and only substitution there is effective in delocalization. The non-bonding orbital of the 2-phenylallyl cation is unaffected by rotation of the phenyl group. The corresponding radical and anion curves thus parallel precisely the cation curve which is shown in Figure 12. There has been apparently no previous estimate of the equilibrium geometry of either the 1-phenyl or 2-phenyl cations. An X-ray structure of a relevant case, the 3-chloro-1,2,3,4-tetraphenylcyclobutenium cation,[48] does show maximum interaction and trend to coplanarity, with the phenyl groups on the termini of the allyl cation. In a theoretical study of the related neutral system, α-methylstyrene, Suzuki extrapolated a twist angle of 33° from the observed spectrum.[44] Favini and Simonetta[45] recalculated Suzuki's value at 36° and by a method of their own arrived at a twist angle of 32°.

Our initial hope was to construct a series of phenyl-substituted cations in which the amount of charge localized at a given carbon could be systematically varied, and the amount of charge delocalized by a planar phenyl group substituted at that site compared to its barrier to rotation by 90°. We could not carry out such a study because nearly all the realistic models we constructed, *e.g.*, the phenylallyl cations, had unavoidable steric problems in the planar geometries. For two of these cases, however, we felt that the steric problems were minor and that the energy barrier could be estimated. These were the *trans*-1-phenylallyl cation and the *trans*-1-phenylpentadienyl cation, for which we extrapolated an unhindered energy for the coplanar geometry on the basis of the 45 and 90° points and a cos^2 θ functional form of the energy. It should be noted that we felt no need to modify the charge delocalization in sterically hindered molecules. The effect of a short H–H contact is electron displacement from the affected hydrogen, so that this hydrogen becomes positively charged. Virtually all the charge is displaced to the adjacent carbon to which the hydrogen is bonded, and in our calculations the effect does not significantly propagate further. Because our charge delocalization is summed over the entire C$_6$H$_5$ unit we felt that it was a fair assumption to presume that the calculated charge delocalization would be very similar to that in a hypothetical unhindered molecule. In Table II we compare charge delocalization and rotation barrier for benzyl, phenylallyl, phenylpentadienyl, and phenylcyclopropenium cations.

The ΔQ values are very roughly in the anticipated

(43) R. F. Bryan, *J. Amer. Chem. Soc.*, **86**, 733 (1964).

(44) H. Suzuki, *Bull. Chem. Soc. Jap.*, **33**, 619 (1960).

(45) G. Favini and M. Simonetta, *Theoret. Chim. Acta*, 1, 294 (1963).

Table II: A Comparison of Charge Delocalization and
Energy Required to Rotate a Phenyl Group by 90°

Cation	ΔE, eV[a]	ΔQ[b]
Benzyl	0.39	0.29
1-Phenylallyl-*trans*	0.21[c]	0.17
1-Phenylpentadienyl-*trans*	0.20[c]	0.12
1-Phenylcyclopropenium	0.00	0.09

[a] $\Delta E = E(\theta = 90°) - E(\theta = 0°)$. [b] $\Delta Q = Q(\theta = 0°) - Q(\theta = 90°)$. [c] Extrapolated, see text for procedure.

ratio. If there is a unit of charge resident at the phenyl-substituted carbon in benzyl, a simple Hückel calculation would put one-half of a unit at each terminal carbon of an allyl system and one-third at each carbon of cyclopropenium and alternate carbons of pentadienyl. The ΔE values clearly show the anomaly of the phenylcyclopropenium species; the comparison with $PhC_5H_6{}^+$ is particularly striking. Whereas the charge delocalization is not much lower in $PhC_3H_2{}^+$ than in $PhC_5H_6{}^+$, the energy barrier has vanished.

One possible explanation of the anomalously flat phenylcyclopropenium potential energy which may be suggested[46] is that the flatness is created by superposition of the normal delocalizing interaction favoring the 0° geometry and another delocalizing interaction involving the σ system of the three-membered ring, operative optimally in the 90° form. In molecular orbital language one describes the stabilization of a carbonium ion adjacent to some π-electron system in terms of the interaction of an empty p orbital and the occupied orbitals of the π system. We illustrate this below for the case of a classical delocalization, such as the "formation" of an allyl cation from an ethylene and a p orbital, and for a nonclassical case, such as 7-norbornenyl cation. These interaction diagrams illustrate a
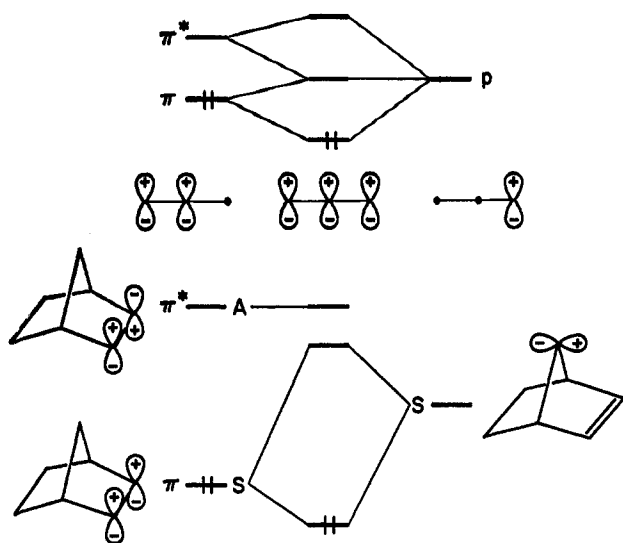

somewhat misleading aspect of the colloquial statement

The Journal of Physical Chemistry

"carbonium ions are stabilized by delocalization." On some reflection it becomes clear that this statement is correct if the phrase "carbonium ion" refers to the molecule as a whole. In fact whereas the stabilization takes place in the π orbitals moving to lower energy as a result of interaction (mixing with p), the carbonium ion center itself, originally p, is actually destabilized by this interaction. It should also be noted how charge transfer enters this molecular orbital picture. A molecular orbital, say π, has originally two electrons. When it is delocalized, it mixes into itself p, becoming of the general form $c_1\pi + c_2p$. There are still two electrons in that molecular orbital, but now they are distributed partly (*i.e.*, less than two) on π, partly on p. It is in this way that transfer of electron density to the carbonium ion center is achieved.

Let us return to phenylcyclopropenium cation. The molecular orbitals of the two systems are sketched below, for a coplanar arrangement. Levels are classified as symmetric or antisymmetric with respect to the perpendicular mirror plane bisecting the molecules.
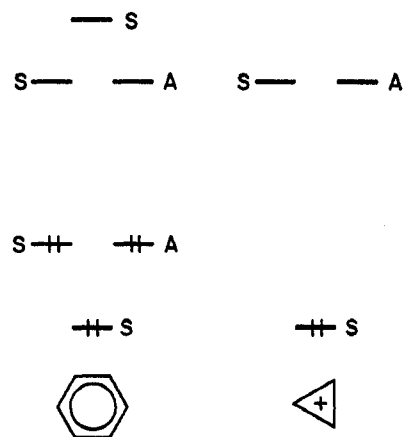

The stabilizing interaction, in the usual perturbation theory manner, is roughly proportional to the square of the overlap of two levels and inversely proportional to the energy separation of these levels. The latter criterion points to the major interaction as being the mixing of unoccupied cyclopropenium levels with occupied benzene levels. The A orbitals mix inefficiently since they have no electron density at the two junctures. The main interaction is that of the S levels drawn below. This interaction decreases as the
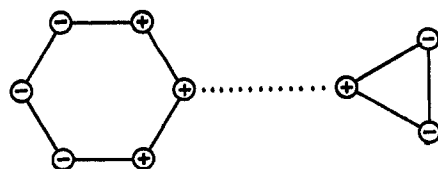
two rings are rotated away from planarity. At $\theta = 90°$ the only interaction is between the π system of one ring and the σ orbitals of the other. The suggestion made

(46) Due to M. J. Goldstein.

here is that cyclopropenium, being a three-membered ring, has a particularly low-lying σ^* orbital which is effective at interacting with the π system of benzene even when the rings are rotated 90°. This unoccupied orbital is the third member of the Walsh set,[47] and the interaction is depicted below. If this explanation is
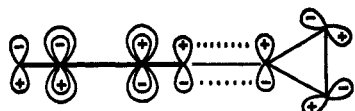
valid, it should manifest itself in the calculations in the form of charge transfer from the π system of benzene to the σ system of cyclopropenium at 90°. That is, whereas in the other molecules the charge transfer should involve π systems only, diminishing as one rotates from coplanarity, in the case of cyclopropenium there should be further electron transfer from phenyl at 90°. Also in the cyclopropenium unit the π system should exhibit normal behavior, but the σ system should grow negative as 90° is approached. The calculated molecular orbitals conform to the above analysis. Thus, whereas in all other 90° cations the S component of the degenerate benzene highest occupied molecular orbital is at an energy slightly higher than its A companion, in phenylcyclopropenium the S level is below the A. However, the charge distributions do not show the anticipated changes, and in fact the σ system of cyclopropenium contributes much more to the charge transfer at 0° than the negligible contribution of the σ system of a simple carbonium ion.

It was suggested to us by B. G. Ramsey that cyclopropenium should be less effective at charge transfer, i.e., delocalization, than tropylium. This judgment is based on the fact that tropylium should be a much better "acceptor" since it has its lowest unoccupied orbital at a considerably lower energy than cyclopropenium. We carried out a perturbation treatment of the interaction of a benzene ring with another π system, based on simple Hückel orbitals for both components. The expression for the energy change is

$$\Delta E \sim \sum_{i}^{occ} \sum_{i'}^{unocc} - \sum_{i'}^{occ} \sum_{i}^{unocc} \frac{(c_1^i c_2^{i'})^2}{\epsilon_{1i} - \epsilon_{2i'}} \qquad (1)$$

where the ϵ_{1i} are the energy levels of one system, $\epsilon_{2i}{}'$ the levels of the other component, and c_1^i and $c_2^{i'}$ are the coefficients of the interacting atomic orbitals of 1 and 2 in molecular orbitals i and i'. The perturbation sum of eq 1 is evaluated in Table III.

The position of cyclopropenium in this series is in good agreement with the trends of the extended Hückel results. They most clearly show that pentadienyl is a bad model for cyclopropenium, since the former, with its nonbonding unoccupied molecular orbital is a much better acceptor, nearly as good as allyl. The perturbation sums for tropylium, cyclopentadienide, and cyclopropenium are all, however, quite close in magnitude

Table III: Perturbation Sum, Which Is Proportional to Stabilization Energy for the Interaction of Benzene with Various π Systems. Simple Hückel Orbitals Are Used for All Molecules

π system	Perturbation sum
Carbonium	0.416
1-Allyl	0.301
1-Pentadienyl	0.277
Tropylium	0.212
Cyclopentadienide	0.206
Cyclopropenium	0.199
2-Allyl	0.186

and so the total flatness of the cyclopropenium curve compared to the obvious trend to planarity in the other two remains anomalous.

In an independent approach to this problem we carried out some Pariser–Parr–Pople calculations on benzyl cation and phenylcyclopropenium cation. The method and parameters were described by us previously,[48] and we only mention here that the SCF version we have devised is particularly useful for studying the torsional behavior of π systems. For benzyl we obtain a delocalization of charge, ΔQ, of 0.490 and an energy barrier at the perpendicular geometry of 2.672. For phenylcyclopropenium cation we calculate a ΔQ of 0.182 and a barrier of 1.216 eV. There are some reasons why the Pariser–Parr–Pople method may not be reliable for cations with varying charge transfer, and we do not trust it greatly in this case.

What about the experimental evidence concerning the geometry of arylcyclopropenium species? The low barrier to twisting that we find for triphenylcyclopropenium is not too large to be overcome by packing forces to produce the observed near-planar crystal structure.[39] It is clear that the stability increment on phenyl substitution calculated from simple Hückel theory[32,33,36] is not paralleled by the actual stabilities of triphenyl-[30] and diphenylcyclopropenium[49,50] ions. It has also been inferred that not much charge is removed by the phenyl group in these carbonium ions.[51] The di- and tripropylcyclopropenium cations are definitely more stable (with respect to the related hydrocarbon) than the phenyl-substituted ions.[35,51] This was an unexpected result, but one consistent with little stabilizing interaction of the cyclopropenium electrons with a phenyl group.

The positive evidence for phenyl interaction, and by inference, stabilization of a coplanar geometry, is mostly

(47) A. D. Walsh, Trans. Faraday Soc., **45**, 179 (1949).

(48) R. Hoffmann, A. Imamura, and G. D. Zeiss, J. Amer. Chem. Soc., **89**, 5215 (1967).

(49) R. Breslow and H. Höver, ibid., **82**, 2644 (1960).

(50) D. G. Farnum and M. Burr, ibid., **82**, 2651 (1960).

(51) R. Breslow, H. Höver, and H. W. Chang, ibid., **84**, 3168 (1962).

Table IV: Highest Occupied (HOMO) and Lowest Unoccupied (LUMO) Molecular Orbital Energy Levels in Electron Volts for the Three Phenyl-Substituted Cyclopropenium Ions, at 0° and 90° Twist of All Phenyl Groups

	$PhC_3H_2{}^+$		$Ph_2C_3H{}^+$		$Ph_3C_3{}^+$	
	0°	90°	0°	90°	0°	90°
LUMO	−9.36	−8.45	−9.52	−8.45	−9.53	−8.65
HOMO	−12.78	−12.39	−12.56	−12.15	−12.34	−12.05
Gap	3.42	3.94	3.04	3.70	2.81	3.45

indirect. There is a progression in stability with phenyl substitution on the cyclopropenium ring. This appears to be indicative of a conjugative interaction, since if there were no such interaction at all and all phenyl rings were twisted 90°, then it could be argued that one would expect the opposite trend, based on an inductive effect argument alone. We have no results bearing on this point. Another argument for some conjugative interaction is based on the appearance of the electronic spectra of $PhC_3H_2{}^+$ and $Ph_2C_3H{}^+$. The latter has a double-peaked absorption band at 293 and 307 nm, log ϵ = 4.60,[35] the former has a similar band somewhat red-shifted.[30] The simplest explanation of the difference of this absorption from that of isolated benzene and cyclopropenium chromophores is in terms of a conjugative interaction. Our calculations, as any one-electron computations, are unreliable in predicting absorption spectra, but trends within a series are generally qualitatively reproduced. The position of the highest occupied and lowest unoccupied levels in the phenyl-cyclopropenium species is listed in Table IV.

The individual levels clearly move in energy with twisting, and the energy gap between filled and unfilled orbitals is greater by 0.5–0.6 eV in the "unconjugated" 90° than in the "conjugated" 0° geometry. Just as with charge delocalization, one has here a manifesta-tion of interaction of cyclopropenium with phenyl, but apparently not one which is "worth" any energy. There is a red shift with increasing phenyl substitutions, and it is there in the 90° geometries as well as the 0°. Table I reveals that, in general, there obtains sizable variation in the extent of charge transfer to a phenyl group even when it is perpendicular to another π system. This should manifest itself in spectral differences in such molecules, even though the two chromophores are formally noninteracting.

In conclusion, we remain puzzled with our calculated result of insensitivity of phenylcyclopropenium to twisting. We do not find the experimental evidence contradicting the calculation, but neither have we uncovered a completely convincing simple argument for this anomaly. Further evidence is needed to decide if the calculation is simply misrepresenting the true energetics of this motion.