not be made until complete geometry optimization studies are made, and the same is true of INDO. In our view, each conformation being compared must be completely geometry optimized with respect to energy and then only those minimized conformations should be compared in stability. Without going through this procedure it is impossible to really see which conformation CNDO/2 (or INDO, etc.) inherently predicts as most stable.

(39) C. U. Pittman, Jr., A. Kress, and L. D. Kispert, *J. Org. Chem.*, **39**, 378 (1974).

(40) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, **87**, 1320, 1326 (1965).

(41) R. Breslow and L. J. Altman, *J. Amer. Chem. Soc.*, **88**, 504 (1966).

(42) M. Gaudemar, *Bull. Soc. Chim. Fr.*, 974 (1962).

(43) A. Streitweiser, *Chem. Rev.*, **56**, 571 (1956).

(44) J. W. Larsen, *J. Amer. Chem. Soc.*, **92**, 5136 (1970).

(45) E. M. Arnett, R. P. Quick, and J. W. Larsen, *J. Amer. Chem. Soc.*, **92**, 3977 (1970).

(46) N. N. Lichtin, *Progr. Phys. Org. Chem.*, **1**, 75 (1963).

(47) N. Deno, J. Bollinger, K. Hafer, J. D. Hodge, and J. J. Houser, *J. Amer. Chem. Soc.*, **85**, 2998 (1963).

(48) C. Jutz and F. Volthenleitner, *Chem. Ber.*, **97**, 29 (1964).

(49) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963); H. C. Brown and J. D. Cleveland, *J. Amer. Chem. Soc.*, **88**, 2052 (1966).

(50) S. W. Tobey, from "Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity," in the Proceedings of the Jerusalem Symposia on Quantum Chemistry and Biochemistry, III, 1971, p 351.

(51) R. Breslow, G. Ryan, and J. T. Groves, *J. Amer. Chem. Soc.*, **92**, 988 (1970).

(52) D. J. Bertelli and T. G. Andrews, Jr., *J. Amer. Chem. Soc.*, **91**, 5280 (1969).

(53) R. Breslow, M. Oda, and J. Pecoraro, *Tetrahedron Lett.*, 4415, 4419 (1972).

(54) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).

(55) P. C. Lauterbur, *Tetrahedron Lett.*, 274 (1961).

(56) G. A. Olah and G. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 1430 (1970).

(57) G. J. Ray, A. K. Colter, and R. J. Kurland, *Chem. Phys. Lett.*, **2**, 324 (1968).

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

INDO Theoretical Studies. VII.[1] Cyclobutadienyl Dications

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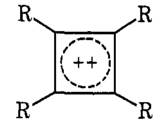
Received July 3, 1973

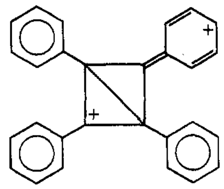
Geometry-optimized INDO calculations have been performed on six cyclobutadienyl dications including $C_4H_4^{2+}$ (3), $C_4F_4^{2+}$ (4), $C_4(CH_3)_4^{2+}$ (5), $C_4(NH_2)_4^{2+}$ (6), $C_4H_3(NH_2)^{2+}$ (7), and $C_4H_3Ph^{2+}$ (8). The magnitude of conjugation by F, NH_2, and Ph groups with the four-membered ring was assessed by examining the calculated π-bond orders, rotational barriers, charge densities, orbital electron densities, and the bond lengths. Within the framework of INDO theory these substituents conjugated strongly to the ring (π effect) while the C–F bonds in 4 and the C–N bonds in 6 and 7 remained polarized toward the substituent. Conjugation to such substituents is stronger in cyclobutadienyl dications than in cyclopropenyl cations. Thus the "aromatic" 2 π system accepts a significant amount of π-electron density from the substituents to increase stability, and "anti-aromatic" destabilization does not appear to be a problem.

Simple molecular orbital theory predicts that planar cyclobutadienyl dications, 1, should be stable delocalized 2 π aromatic systems having 2β units of resonance energy.[3] In contrast to the 6 π cyclobutadienyl dianion, the dication should be more stable because its double positive charge will lower the energy of the bonding orbitals. Furthermore, the highest π orbitals of the dication are not degenerate as they are in the cyclobutadiene; thus they would not be subject to Jahn–Teller distortion.



1

Since 1960 a number of unsuccessful attempts to prepare this class of dications appeared.[4-7] However, in 1969 Olah, *et al.*,[8] reported the successful generation of the tetramethylcyclobutadienyl dication upon addition of tetramethyl-2,3-dichlorocyclobutene to SbF_5–SO_2 at −78°. The pmr of the dication exhibited a sharp singlet at δ 3.68, and it was stable at −78° in solution for at least 2 weeks. The ^{13}C spectrum exhibited ring carbon absorption at −14.4 ppm (from CS_2),[8] which agreed with that predicted based on the linear relationship of measured ^{13}C shifts for $C_5H_5^-$, C_6H_6, $C_7H_7^+$, and $C_8H_8^{2-}$ with a slope of 166 ppm per π electron.[9] Shortly thereafter, Olah and Mateescu[10] reported the generation of the tetraphenylcyclobutadienyl dication from 3,4-dibromotetraphenylcyclobutene in SbF_5–SO_2 at −60° (^{13}C δ +17.6 for ring carbons). HMO calculations[10] predicted π-bond orders of 0.45 between ring carbons and 0.47 between ring and phenyl carbons, and a π-electron density of 0.71 at each ring carbon. Thus the calculations suggested a significant contribution of canonical forms such as 2, with charge delocalization into the phenyl rings.



2

No systematic theoretical study of cyclobutadienyl dications has appeared. In order to study the effects of substituents on the bonding in this class of dications, we performed INDO[11,12] calculations on the parent cyclobutadienyl dication (3) and the tetrafluoro- (4), the tetramethyl- (5), the tetraamino- (6), the monoamino- (7), and the monophenylcyclobutadienyl (8) dications. In these calculations the bond lengths and angles of the ring carbons and the substituent atoms (relative to the four-membered ring) were optimized in a systematic fashion.[13,14] In particular, we examined the extent of delocalization into substituents, in view of the observation that alkyl groups stabilize the 2 π cyclopropenyl cations more than phenyl groups do.[15-17] This anomalous stabilizing behavior has led to extensive discussion in the literature of whether or not cyclopropenyl cations were less susceptible to resonance stabilization than traditional open-shell carbonium ions.[10,15-19] Extension of this question to the 2 π cyclobutadienyl dications is of obvious interest.

Throughout this paper we shall qualitatively represent the results of the INDO calculations in terms of ground-state valence bond resonance hybrids. This is done as a convenient method of representing resonance contributions of various functional groups and to compare the ef-

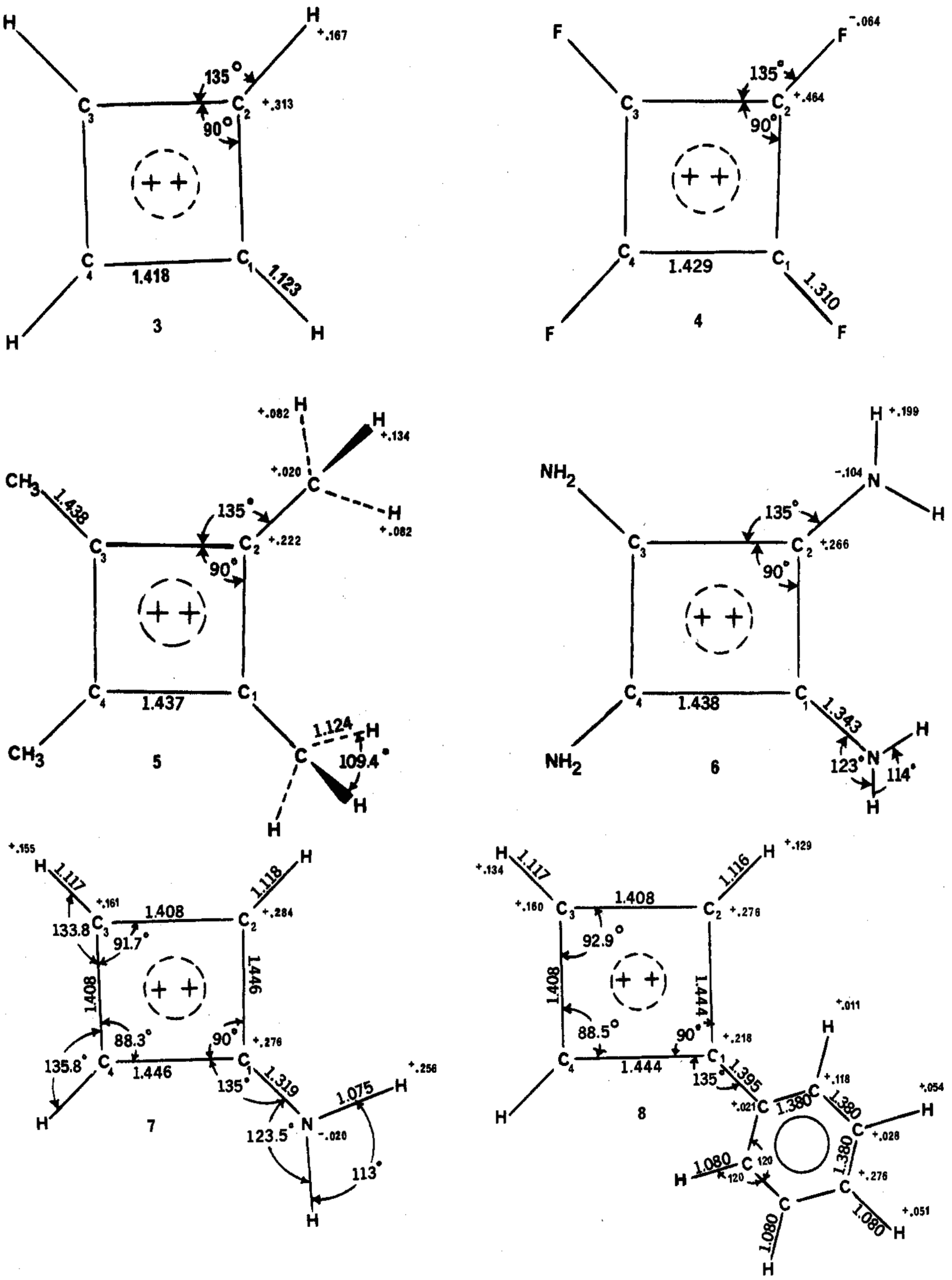

3 4 5 6 7 8

Figure 1. Calculated geometries and charge densities of cyclobutadienyl dications 3–8.

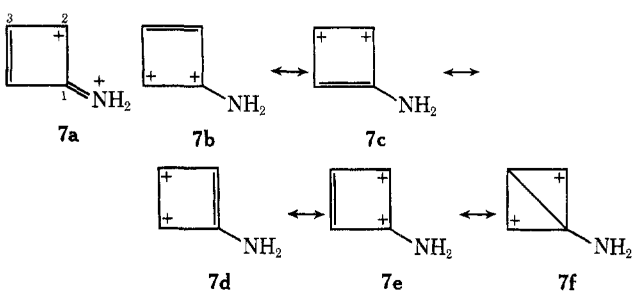
fects of functional groups. However, a recent *ab initio* valence bond calculation of benzene by Norbeck and Gallup[20] pointed out that the relative importance of specific valence bond functions has, in the past, been based almost entirely on empirical and semiempirical calculations. They found that singly polar functions are remarkably stable and of surprising importance in their calculation. The authors stated that the effect that their results have on existing resonance concepts was, at present, unknown.

Results and Discussion

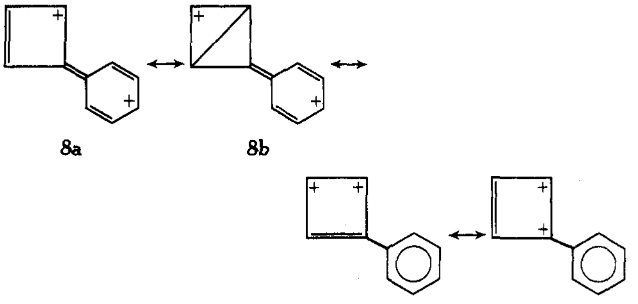
The program CNINDO (QCPE No. 141)[21] was modified for use on a Univac 1108.[1] Structures were generated using model builder program QCPE No. 135. The calculated optimized geometries of dications 3–8 are summarized in Figure 1 along with the charge densities at each atom.

As expected, 3–6 have symmetrical square planar structures (D_{4h} symmetry). Both the monoamino- (7) and monophenylcyclobutadienyl dication (8) exhibit a distorted planar ring geometry with the C_1–C_2 length greater, in both, than the C_2–C_3 length. Furthermore, the charge density at $C_2 > C_1 > C_3$ in both 7 and 8. Thus, in 7 smaller contributions by hybrid structures **7c** and **7d** occur *vs.* **7e**, **7b**, and **7a**. Likewise, in 8 the contributions by **8a** and **8d** are more important than those of **8b** and **8c**. Substantial charge delocalization into both the amino (in 7) and phenyl (in 8) groups also takes place. Delocalization occurs most strongly to the para position in 8; yet substantial charge is found at the ortho carbons. In 7 the nitrogen is much less negatively charged than expected for a nitrogen bonded to a neutral carbon within the INDO framework,[12] and the amino hydrogens bear a large positive charge (+0.26 each).

Further evidence that both the amino and phenyl rings are strongly conjugated to the ring in 7 and 8 is obtained by examining the π-bond orders, group rotational barriers, and the π-orbital electron distributions. The C–N π-bond order in 7 is 0.820 while that of the ring to phenyl C–C



7a **7b** **7c** **7d** **7e** **7f**

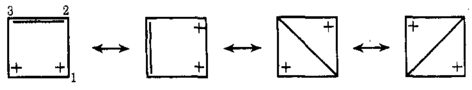


8a **8b** **8c** **8d**

bond in 8 is 0.638. The calculated rotational barriers[22] of the amino and phenyl groups are 60 and 21 kcal/mol, respectively.[23] Finally, in 7 the nitrogen p_y orbital is occupied by only 1.42 electrons, indicative of strong back π donation of electron density to the cyclobutadienyl ring. In 8 the values of $q(\mathrm{p}_y)$ match the pattern exhibited by the total charge density distribution. The values of $q(\mathrm{p}_y)$ are C_1 = 0.723, C_2 = 0.505, C_3 = 0.776, bound phenyl carbon = 1.029, C_{ortho} = 0.876, C_{meta} = 0.977, C_{para} = 0.505. The majority of the π-electron density is donated to the four-membered ring from the ortho and para positions. Thus, in 7 and 8 the NH_2 and phenyl groups are strongly conjugated to the cyclobutadienyl ring.

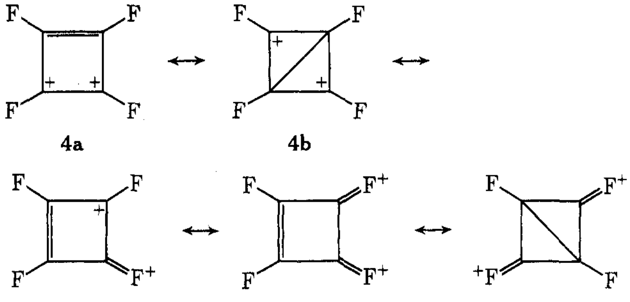
The geometrical distorsion of 7 and 8 is also reflected in the π_y bond orders in the ring. These orders are for 7 C_1–C_2 = 0.33, C_2–C_3 = 0.617, C_1–C_3 = 0.239, and C_2–C_4 = 0.516; and for 8 C_1–C_2 = 0.359, C_2–C_3 = 0.601, C_1–C_3 = 0.263, C_2–C_4 = 0.504. This further supports smaller contributions by hybride structures **7c**, **7d**, and **7f** relative to **7a**, **7b**, and **7e**.

Symmetrically substituted dications 3–6 are aromatic delocalized systems. The parent ion of this system, 3, has a symmetrical charge distribution (+0.313 at each carbon), short equivalent C–C bond distances (1.418 Å), and equal π-bond orders (π_y C_1–C_2 = C_2–C_3 = C_1–C_3 = 0.50). The equality of the C_1–C_3 π-bond order with that of C_1–C_2 can be represented by the contribution of resonance hybrid **3c** and **3d**. It must be remembered that in **3c** and **3d** the bond across the ring is a π bond and not a σ bond. It should be pointed out that the strict equality in this special 2 π case is determined by symmetry, because only the lowest molecular orbital is occupied. It has the form $\Psi = \frac{1}{2}\phi_1 + \phi_2 + \phi_3 + \phi_4)$ when the overlap integrals are ignored (*i.e.*, $S_{\mu\nu}$ integrals are neglected during MO normalization). Only when more π electrons are present do the effects of $H_{\mu\nu} = B°_{AB}S_{\mu\nu}$ enter in.



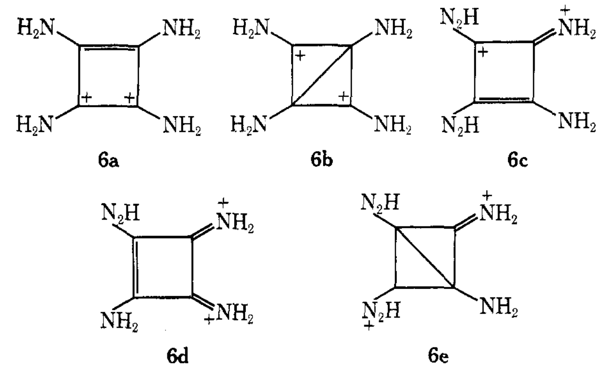
3a **3b** **3c** **3d**

In both 4 and 6 the substituents, F and NH_2, respectively, are conjugated to the ring providing π-electron density. This reduces the ring π-bond orders. For example, in 3 the C–F π-bond order is 0.48 while the C_1–C_2 order has decreased to 0.47 (*vs.* 0.50 in 3) and the C_1–C_3 order is reduced to 0.39. The increase in electron density in the carbon π orbitals [$q(C_y)$) = 0.68 for 4 *vs.* $q(C(\mathrm{p}_y))$ = 0.50 for 3] results largely from back π donation from the filled flourine [$q(F(\mathrm{p}_y))$ = 1.82] p_y orbitals. The C–F σ bond, on the other hand, is strongly polarized toward fluorine [$q(C(\mathrm{p}_y))$ = 0.78, $q(F(\mathrm{p}_y))$ = 1.33]. The calculated fluorine–carbon conjugation is greater in 4 than in the trifluorocyclopropenyl cation. Strong contribution by hybrid structures **4c** and **4d** is indicated and structures **4b** and **4e** make a significant contribution. Qualitative symmetry arguments show that MO IV is less important in the ring carbons than MO's I–III and V. This results in the C_1–C_3 order reduced relative to C_1–C_2.



4a **4b** **4c** **4d** **4e**

Conjugation of the amino groups of 6 with the ring is indicated by a large C–N π-bond order (0.62) and reduced ring π-bond orders (C_1–C_2 = 0.44 and C_1–C_3 = 0.28) relative to 3. The π-electron density on the ring has sharply increased [$q(C(\mathrm{p}_y))$ = +0.85 *vs.* 0.50 in 3] to a total of 3.4 π electrons *vs.* 2 in 3. The nitrogen provides electron density from its π orbital [$q(N(\mathrm{p}_y))$ = 1.65] while, inductively, the nitrogen is still electron withdrawing as indicated by the polarization of the C–N σ bond toward nitrogen [$q(C(\mathrm{p}_z))$ = 0.86, $q(N(\mathrm{p}_z))$ = 1.08]. Furthermore, a large out-of-plane rotational barrier of 29 kcal/mol is calculated for the amino groups in 6.[24] It is quite clear that hybrid structures such as **6c** and **6d** contribute strongly while structures such as **6b** make less contribution than their analogs do in 3 and 4.

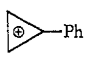
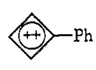
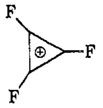
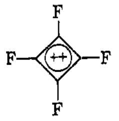
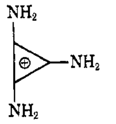
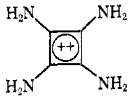


6a **6b** **6c** **6d** **6e**

Methyl groups of 5 donate electron density to the ring's π system [$q(C(\mathrm{p}_y))$ = 0.65 *vs.* 0.50 for 3 and 0.68 for 4]. This is a hyperconjugative interaction, as evidenced by the larger charge on the methyl hydrogens perpendicular to the ring plane (+0.134) relative to the others (+0.082). This donation results in charge buildup on the methyl hydrogens and decreased ring π-bond orders relative to 3 (*i.e.*, C_1–C_2 = 0.47, C_1–C_3 = 0.39). The C_1–CH_3 σ bonds are nonpolar [$q(C(\mathrm{p}_y))$ = 1.07 and 1.02 (methyl carbon)]. This nonpolarity reduces the total charge density of the ring carbons of 5 (+0.201) relative to its fluoro analog 4 (+0.464).

A clear picture of the bonding in cyclobutadienyl dications emerges from calculations in the INDO framework. Substituents such as fluorine, phenyl and particularly amino groups strongly back π donate electron density to

Table I
Calculated Quantities Reflecting Substituent Conjugation in Cyclopropenyl Cations *vs.* Cyclobutadienyl Dications

Species	π-Bond orders C_{ring}–sub. bond (C_{ring}–C_{ring})	Rotational barrier C_{ring}–sub. bond	Bond length in Å about C_{ring}–sub. bond	q-4 of C_1	$q(C_1(p_y))$ ring carbon
	0.408 (C_1–C_2 = 0.581) (C_2–C_3 = 0.530)	2.0	1.40	+0.230	0.697 C_1 0.726 C_2, C_3
	0.638 (C_1–C_2 = 0.359) (C_2–C_3 = 0.601)	21.0	1.395	+0.218	0.769 C_1 0.516 C_2 0.782 C_3
	0.339		1.32	+0.310	0.759
	0.480 (0.47)		1.31	+0.464	0.681
	0.453 (0.576)	13.9	1.361	+0.185	0.861
	0.622 (0.44)	29.0	1.343	+0.266	0.854

the four-membered ring's carbons. As the number of conjugating substituents decreases, the demand for such electron donation by the remaining substituents increases (*i.e.*, compare the rotation barriers and π-bond orders of 6 and 7). This conjugation increases the electron density in the four-membered ring's π cloud. This effect is stronger for cyclobutadienyl dications than it is for cyclopropenyl cations. For example, calculated rotational barriers, π-bond orders, and bond lengths support this concept (see Table I). It is impossible to separate the two effects expected to favor this behavior. They are (1) the increased charge density at the ring carbons in the dication series which results in a decreased number of π electrons per ring carbon [$q(C(p_y))$ = 0.5 for 3 *vs.* 0.667 for the cyclopropenyl cation[1]] and (2) the increase in the ring angles from 60 to 90° makes it easier to form exo double bonds to the ring in the cyclobutadienyl dication series. Both effects favor stroger conjugation to substituents in cyclobutadienyl dications.

Like cyclopropenyl cations, the calculated HOMO to LUMO transitions for cyclobutadienyl dications occur at high energies and at wavelengths below 200 nm (84 nm for **3**, 88 nm for **4**, 121 nm for **5**, and 116 nm for **6**). While the absolute values may not be correct, INDO predicts that substituted cyclobutadienyl dications will absorb at longer wavelengths than their cyclopropenyl counterparts.[25]

The separation of π and σ systems provided by INDO calculations should prove useful in future studies of these dications. For example, Olah[10] extended the Spiescke-Schneider correlation[9] of the ^{13}C chemical shifts with the aromatic π-electron densities for the tetramethyl- and tetraphenylcyclobutadienyl dications. In that study, values of the π densities were calculated by simple Hückel MO theory. These values differ markedly from those calculated by INDO [*i.e.*, $q(C(p_y)$ for the ring carbons is 0.64 by INDO and 0.50 by HMO for the tetramethylcyclobutadienyl dication].

Acknowledgments. This work was partially supported by the University of Alabama Research Committee Project Grant No. 672 (to C. U. P.). The University of Alabama Computer Center generously provided free computer time, enabling completion of these studies.

Registry No. 3, 12240-33-4; **4,** 49585-81-1; **5,** 24721-10-6; **6,** 49585-83-3; **7,** 49598-07-4; **8,** 49598-08-5.

References and Notes

(1) For previous papers in this series see C. U. Pittman, Jr., A. Kress, T. B. Patterson, P. Walton, and L. D. Kispert, *J. Org. Chem.*, **39**, 378 (1974), and reference 1 of that paper.
(2) Summer research participant.
(3) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," Academic Press, New York, N. Y., 1967, pp 122–127, contains a review of early work.
(4) D. G. Farnum, M. A. T. Heybey, and B. Webster, *J. Amer. Chem. Soc.*, **86**, 673 (1964); *Tetrahedron Lett.*, 307 (1963).
(5) R. F. Bryan, *J. Amer. Chem. Soc.*, **86**, 733 (1964).
(6) H. H. Freedman and A. M. Frantz, *J. Amer. Chem. Soc.*, **84**, 4165 (1962).
(7) T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, **86**, 1600 (1964).
(8) G. A. Olah, J. M. Bollinger, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3667 (1969).
(9) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).
(10) G. A. Olah and G. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 1430 (1970).
(11) A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).
(12) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.
(13) Each bond length and angle was minimized with respect to all others in the system using an iterative approach to the optimum geometry.
(14) An alternative method, the simplex approach, was available, but it demanded substantially greater computer times in our hands. The simplex program was kindly supplied by Professor M. J. S. Dewar and has been used previously by his group; see M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.*, **94**, 5296 (1972).
(15) R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2367 (1961).
(16) R. Breslow, J. Lockhart, and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2375 (1961).
(17) R. Breslow, H. Höver, and H. W. Chang, *J. Amer. Chem. Soc.*, **84**, 3168 (1962).
(18) (a) D. G. Farnum, A. Mostashari, and A. A. Hagedorn, III, *J. Org. Chem.*, **36**, 698 (1971); (b) D. G. Farnum and C. F. Wilcox, *J. Amer. Chem. Soc.*, **89**, 5369 (1967).
(19) R. Hoffman, R. Bissell, and D. G. Farnum, *J. Phys. Chem.*, **73**, 1789 (1969).

(20) J. M. Norbeck and G. A. Gallup, *J. Amer. Chem. Soc.*, **95**, 4460 (1973).

(21) Obtained from the Quantum Chemistry Program Exchange, Indiana University.

(22) The most unstable conformation is 90° out of plane in both **7** and **8**.

(23) While values calculated by INDO theory could be greater than barriers determined experimentally, the trends are clear. Such barriers should be strictly compared within a related series of optimized structures.

(24) This is the barrier for the rotation of a single NH_2 group while the other three remain in the plane.

(25) Tables of the MO energy levels for species **3–8** are available on request from the authors. Configuration interaction was not used in calculations of the above transitions.

Mesitylation and Phenylation of Picolyl Anions by the SRN1 Mechanism[1]

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Received September 5, 1973

The 2- and 4-picolyl anions are arylated, to form arylmethylpyridines, by chlorobenzene, phenyltrimethylammonium ion, and 2-bromomesitylene under stimulation by potassium metal or near-ultraviolet light. These reactions are believed to occur by the SRN1 mechanism. The 2- and 4-picolyl anions are also phenylated in reactions with bromo- and iodobenzene that probably occur in part by the benzyne and in part by the SRN1 mechanism.

The arylation of ketone enolate ions,[3] α-cyanoalkyl anions,[4] and anions derived from several hydrocarbons[3c] *via* the recently discovered SRN1 mechanism[5-7] has been described.

This mechanism,[6] which is sketched in Scheme I for reaction of a carbanion with an aromatic substrate, is initiated by electron transfer (step 1) to the substrate, forming a radical anion. If the electron donor is a solvated electron, the residue is merely solvent. If the electron is donated by an anion, under thermal[5a] or photostimulation,[3b] the residue is a radical. In step 2, the radical anion of the substrate ejects a nucleofugic substituent, and an aryl radical is formed. This radical, in step 3, combines with the carbanion to form a new radical anion, which is usually not a particularly stable species. One of the ways in which it can gain stabilization is to transfer its excess electron to another substrate molecule (step 4). One product of that step is the radical anion which is a reactant in step 2, and thus steps 2, 3, and 4 constitute the propagation cycle of a chain mechanism. There are, of course, also termination steps.

Scheme I

$$\text{electron donor} + \text{ArX} \longrightarrow [\text{ArX}]\cdot^- + \text{residue} \qquad (1)$$

$$[\text{ArX}]\cdot^- \longrightarrow \text{Ar}\cdot + \text{X}^- \qquad (2)$$

$$\text{Ar}\cdot + \text{R:}^- \longrightarrow [\text{ArR}]\cdot^- \qquad (3)$$

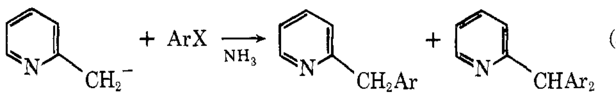
$$[\text{ArR}]\cdot^- + \text{ArX} \longrightarrow \text{ArR} + [\text{ArX}]\cdot^- \qquad (4)$$

It is noteworthy that, although steps 2, 3, and 4 involve radical and radical anion intermediates, the net input is substrate ArX plus anion $R:^-$ and the net output substitution product ArR with by-product X^-; thus, in effect, the reaction is a nucleophilic substitution.

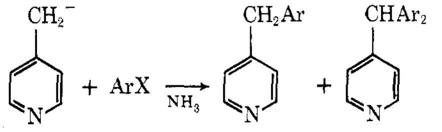
The present research extends studies of aromatic SRN1 reactions to include picolyl anion nucleophiles. The 2- and 4-picolyl anions are obtained by the action of KNH_2 on 2- and 4-picoline, respectively, in liquid ammonia solution.[8]

Results

We find that the 2- and 4-picolyl anions are arylated under conditions conducive to the SRN1 mechanism, according to the general pattern of eq 5 and 6. Our experiments are summarized in Table I.



(5)



(6)

Runs 1, 5, 7, and 9 were conducted either in the dark (in a flask wrapped with aluminum foil) or with exposure to the usual diffuse illumination of the laboratory, without stimulation by solvated electrons. Under these conditions, bromobenzene and the 2-picolyl anion (run 5) reacted to form arylation products in a total yield of 69%, conforming to the general pattern of eq 5. Iodobenzene and the 4-picolyl anion (run 1) formed 14% of 4-benzylpyridine in a much shorter reaction time and at a much lower temperature. However, chlorobenzene (run 7) and phenyltrimethylammonium ion (run 9) were essentially unreactive with the 2-picolyl anion.

It is probable that, in runs 1 and 5, reaction occurred by the benzyne mechanism.[9,10] The 2- and 4-picolyl anions have pK_a's of approximately 31 and 29, respectively, not far from $pK_a = 33.2$ for amide ion.[8] It is therefore not unreasonable that the picolyl anions or amide ion in equilibrium with them should bring about benzyne formation on reaction with iodo- and bromobenzene, which are particularly prone to form benzyne on reaction with strong bases.[9] On the other hand, chlorobenzene has a lesser and phenyltrimethylammonium ion a much lesser tendency to form benzyne on reaction with amide ion in ammonia.[9,14]

Because of the considerable reactivity of iodo- and bromobenzene with the picolyl anions in unstimulated reactions, the mechanisms of their reactions stimulated by potassium metal (runs 2 and 3) or irradiation (run 6) are uncertain. A mixture of benzyne and SRN1 mechanisms seems probable.

On the other hand, for reasons mentioned it is likely that the potassium metal stimulated reaction of chlorobenzene (run 8) and the photostimulated reaction of phenyltrimethylammonium ion (run 10), both with the 2-picolyl anion, occur largely or entirely by the SRN1 mechanism. These runs formed 2-benzylpyridine in yields of 48 and 66%, respectively. Very similar is the photostimulated phenylation of the 4-picolyl anion by phenyltrimethylammonium ion (run 4), which gave 88% of 4-benzylpyridine.

As a means of avoiding absolutely the possibility of the benzyne mechanism as a complication, we turned our attention to arylation with 2-bromomesitylene (**1**), which