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Structure and Reactivity of Aromatic σ-Complexes (Cyclohexadienylium Ions): A Correlated Experimental and Theoretical Study

F. Effenberger,*[†,‡] F. Reisinger,[‡] K. H. Schönwälder,[‡] P. Bäuerle,[‡] J. J. Stezowski,*[‡] K. H. Jogun,[‡] K. Schöllkopf,[‡] and W.-D. Stohrer*[⊥]

Contribution from the Institut für Organische Chemie der Universität Stuttgart, Pfaffenwaldring 55, 7000 Stuttgart 80, Federal Republic of Germany, and Studiengang Chemie der Universität Bremen, 2800 Bremen, Federal Republic of Germany. *Received June 3, 1986*

Abstract: Steric and electronic properties for a series of σ-complexes have been examined by experimental and theoretical techniques. Crystal structures for three 2,4,6-tripyrrolidinocyclohexadienylium salts **3a**, **3b**, and **4a** and for 1-methyl-2,4,6-tripyrrolidinobenzene **5** are reported. With respect to the cyclohexadienylium ring, the H,H σ-complexes, **3**, display a planar conformation whereas σ-complexes **4** and **6** are bent. Steric interactions force the larger substituents of the tetrahedral carbon atom in **4** and **6** into the pseudoaxial position. The results of EH, MNDO, and 3-21G calculations are in agreement with the crystal structure determinations for σ-complexes **3**, **4**, and **6**. Calculations performed for other σ-complexes indicate that the ring conformation for σ-complexes with small substituents in the 2- and 6-positions should be planar even in cases with different substituents on the tetrahedral carbon atom; with larger substituents, a bent conformation is favored with the larger substituent at C1 axial. The activation energy for planarization of the bent structure is fairly high, and it is even higher for inversion. For stereoelectronic reasons, only the ligand in the axial position of bent σ-complexes can dissociate during rearomatization. Thus the stability and reactivity of σ-complexes are strongly dependent on their conformation. The large differences in pK_a values of planar and nonplanar σ-complexes, as well as the unexpectedly high stability of phloroglucinophane σ-complexes, can be explained by the high inversion energy for the formation of the σ-complexes with the proton as the leaving group in the axial position.

Electrophilic substitution (Scheme I) plays an important role in the chemistry of aromatic compounds. With few exceptions,[1] the intermediate σ-complexes, **2**, have not been isolated and characterized. Consequently, little is known about the structure and properties of this transient species.

In addition to the observed rearomatization of the σ-complexes to either educt **1a** and/or product **1b**, competing reactions are possible and in a few cases are known.[2-8] The factors that determine the alternative reaction pathways are not well understood. It is, however, very probable that the conformations of **2** (Scheme II) play an important role in determining their chemistry. For example, in planar conformation **2B**, the C–R and C–R′ bonds are conformationally equivalent, whereas in the nonplanar conformations **2A** and **2C**, the equatorial and axial bonds may be expected to show different reactivity.

Drawing on the results of crystal structure determinations combined with theoretical calculations, we have examined the steric and electronic effects of substituents on the conformations accessible to σ-complexes and the influence of conformation on their chemical properties.

We report crystal structure determinations for 2,4,6-tripyrrolidinocyclohexadienylium perchlorate (**3a**), 2,4,6-tripyrrolidinocyclohexadienylium bromide (**3b**), 1-methyl-2,4,6-tripyrrolidinocyclohexadienylium perchlorate (**4a**), and 1-methyl-2,4,6-tripyrrolidinobenzene (**5**). The crystal structure of **5** was determined to obtain experimental data suitable for assessing the steric contributions to the conformations of *o,o′*-pyrrolidino substituted benzenes, the parent of the σ-complexes **3**, **4a**, and **6**. Structural data for 1-bromo-2,4,6-tripyrrolidinocyclohexadienylium bromide (**6**),[9] heptamethylcyclohexdienylium tetrachloroaluminate (**7a**),[10] and 1-phenylhexamethylcyclohexadienylium tetrachloroaluminate (**7b**)[11] are also considered in the comparison of theoretical and experimental results.

Experimental Procedures and Theoretical Concepts

The crystallographic data for the crystals of **3**, **4a**, and **5** are characterized in Table I. Diffraction intensities were measured with a Syntex PI autodiffractometer (Mo Kα radiation, $\lambda = 0.71069$ Å) operating in an ω-scan mode (see Table I for further details). Three reference reflections, measured periodically, were used to monitor the stability of each crystal over the course of the experiment; where appropriate (Table I) corrections were made for variations. Data were corrected for Lorentz and polarization effects but not for absorption.

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[‡] Institut für Organische Chemie der Universität Stuttgart.

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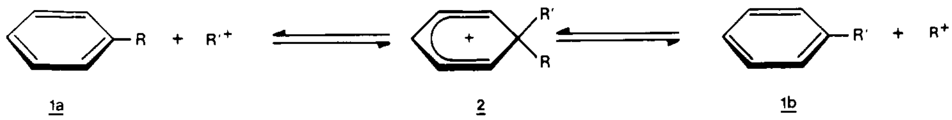
Table I. Characterization of the Experimental Crstallographic Parameters

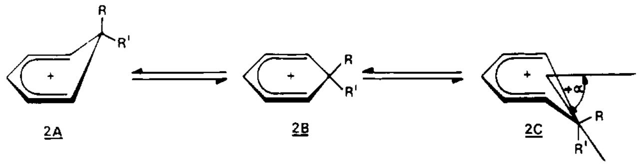
	3a	3b	4a	5
space group	$Pn2_1a$	$P2_1/c$	$P2_1/c$	$P2_1/n$
crystal temp, K	297 (2)	~120	~120	~120
lattice parameters				
a, Å	20.870 (2)	15.949 (23)	8.491 (1)	11.037 (1)
b, Å	7.6773 (8)	14.204 (3)	13.992 (1)	7.936 (1)
c, Å	12.279 (2)	16.678 (18)	16.571 (2)	18.992 (2)
α, deg	90	90	90	90
β, deg	90	114.7 (1)	96.31 (1)	92.00 (1)
γ, deg	90	90	90	90
no. of 2θ values	15	15	63	45
range, deg	25.54–37.27	26.22–32.49	30.40–51.69	23.95–47.57
chemical formula	$(C_{18}H_{28}N_3)^+ClO_4^-$	$(C_{18}H_{28}N_3)^+Br^-$	$(C_{19}H_{30}N_3)^+ClO_4^-$	$C_{19}H_{29}N_3$
Z	4	8	4	4
intensity data set				
resolution,[a] deg	45	55	80	70
no. of unique data	1373	7381	12231	7173
no. of obsd data	918	5481	6917	4008
max dev in ref reflns, %	5	11	2	10

[a] Maximum 2θ value for monochromatized Mo Kα radiation.

Scheme I



Scheme II



The initial structural models, determined by direct methods[12] were developed[13] by difference Fourier and least-squares refinement techniques. The refinements are characterized in Table II.

The theoretical calculations considered both steric and electronic effects with use of ab initio, extended Hückel (EH), and MNDO techniques.

Results and Discussion

Refined fractional atomic coordinates for the crystal structures are contained in Table III; additional data are available.[14] Selected bond distances, bond angles, and torsion angles are presented in Tables IV–VI, respectively. Stereoscopic projections[15] illustrating molecular conformations and the atom labeling schemes are presented in Figure 1.

Analysis of the Crystal Structures. The crystal structures reported here present three different chemical moieties relevant to understanding the structural properties of σ-complexes **2**. On the basis of comparison of the three molecular species, we believe these structures provide insight into the effects governing the conformation of σ-complexes in general and provide experimental results useful for evaluation of the theoretical calculations described below.

There are three independent observations of the R = R′ = H cation, one from **3a** and two from **3b**. The generally poorer quality of the crystals and the resulting lower precision in the bonding parameters for both examples of **3** compared to that for **4a** and **5** is traceable to disorder, primarily in CH_2 moieties of the pyrrolidino groups. Consequently, bonding parameters have been averaged assuming C_s molecular symmetry (Scheme IV, Table VII).

Comparison of the bonding parameters in Table VII supports conclusions about which structural effects are largely steric, largely electronic in nature, or most likely determined by a combination of the two.

The C1–Cα bond distances in **3** and **4a** differ by 0.014 Å. In **5**, the same average bond distance is 0.011 Å longer than the remaining aromatic C–C values. Similar differences in the aromatic C–C bond distances have also been reported for 2,4,6-trinitro-2′,4′,6′-tripyrrolidinobiphenyl.[16] Our MNDO calculations for the 4-amino-2,6-bis(methylamino)cyclohexadienylium complex, **8a** and the 4-amino-2,6-bis(methylamino)-1-methylcyclohexadienylium complex, **8b** (see Scheme V) (used as models for **3** and **4a**), result in bond lengths for C1–Cα which differ by 0.012 Å, which is in good agreement with the experimental values (see Table X).

We conclude that the C1–Cα bond in **4a** is lengthened because of steric interaction between the methyl group and the two *o*-pyrrolidino substituents. This conclusion is supported by the observation that this difference from our MNDO calculations for the corresponding parent compound (without pyrrolidino substituents), $C_6H_7^+$, and its methyl analogue is only 0.007 Å.

Comparison of the bond distances reveals two effects which appear to be largely electronic in nature. The first concerns the bond distances within the pentadienylium system. The Cα–Cβ bonds (1.378 Å in **3** and 1.383 Å in **4a**) are significantly shorter than the Cβ–Cγ bonds (1.423 Å in **3** and 1.424 Å in **4a**) (see Table VII). This trend, as well as the lengthening of the C1–Cα bonds compared to benzene, is also found in theoretical calculations for the parent σ-complex, $C_6H_7^+$. Semiempirical calculations with CNDO/2-FK,[17] MINDO/2′,[18] MINDO/3,[19] MNDO (this work), and our ab initio calculations with use of a 3-21G basis employing

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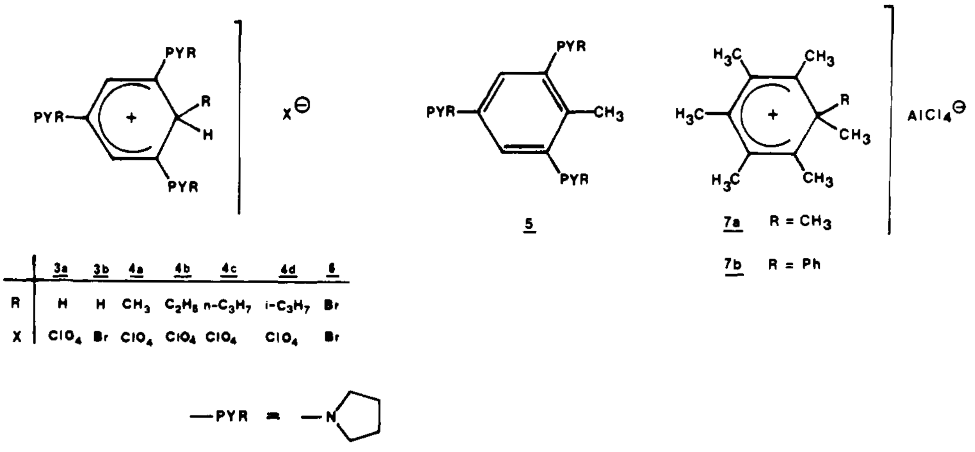
Scheme III



	3a	3b	4a	4b	4c	4d	6
R	H	H	CH_3	C_2H_5	n-C_3H_7	i-C_3H_7	Br
X	ClO_4	Br	ClO_4	ClO_4	ClO_4	ClO_4	Br

Scheme IV

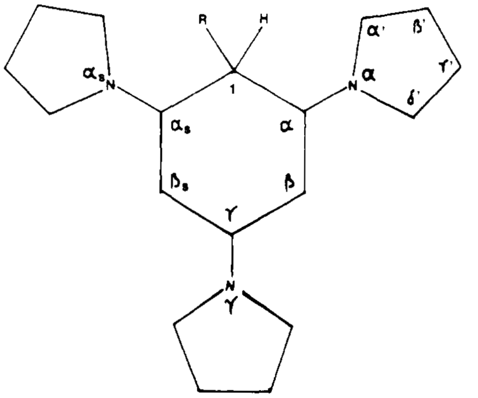


Table II. Characterization of the Crystal Structure Refinements

	3a	3b	4a	5
R	0.094	0.082	0.049	0.048
R_w	0.119	0.100	0.068	0.064
no. of variables	235	386	364	315
no. of contributing reflns[a]	1234	6667	9985	5845
weighting scheme[b]				
a	0.10	0.15	0.0125	0.0125
b	0.003	0.0005	0.001	0.0025
c	6×10^{-7}	1×10^{-8}		
d	4	4		
σ[c]	1.31	1.47	1.08	0.92

[a] Reflections classified as "unobserved" for which the calculated intensities were greater than the cutt-off value, $I \leq 3\sigma(I)$, were used in the refinement. [b] The weighting scheme used was $w = [\sigma^2(F) + aF + bF^2 + cF^d]^{-1}$. [c] σ is the estimated standard deviation in an observation of unit weight.

optimization of geometry gave the following bond lengths: Cα–Cβ = 1.395, 1.390, 1.383, 1.382, and 1.352 Å, Cβ–Cγ = 1.446, 1.424, 1.420, 1.426, and 1.407 Å, and C1–Cα = 1.501, 1.478, 1.476, 1.500, and 1.479 Å, respectively. Our MNDO calculations for **8a** and **8b** indicate that the Cα–Cβ is 0.043 and 0.038 Å shorter than the Cβ–Cγ bond which is in good agreement with the experimental differences of 0.045 Å for **3** and 0.041 Å for **4a**.

The second is the significant increase in the through conjugation of the pentadienylium system to the two α-nitrogen atoms. The Cα–Nα (and the symmetry related $C\alpha_\sigma$–$N\alpha_s$) bond distances in σ-complexes **3** and **4a** are 0.063 and 0.061 Å shorter than in the neutral molecule, **5** (see Table VII). Similarly, although there is evidence for through conjugation in the para position of **5**, it is obviously more pronounced in **3** and **4a**, for which the Cγ–Nγ bond distances are 0.03 Å shorter than in **5**.

The intraring pyrrolidino N–C and C–C bond distances in all three types of complexes are very similar. The average C–C bond distance in **3** is shortened by the conformational disorder of the β′ and γ′ CH_2 residues of the rings. This effect is normal and is also reflected in the large deviation in the average bond distance.

The average bond angles also display effects consistent with the above analysis. For example, the Cα–Nα–Cδ′ bond angle is approximately 5° larger in the σ-complexes than in **5**. Similarly the sum of the C–Nα–C bond angles in **3** and **4a** is each 359.9°, compared with only 342.8° for **5** (see Table VII). These observations are all consistent with a greater degree of through conjugation to the ortho substituents in the σ-complexes than in the aromatic parent molecules.

Steric effects are also detectable in the bond angles. For example, the exocyclic Cα–Nα–Cα′ angle increase on going from **3** to **4a**, as does the angle C1–Cα–Nα.

There are interesting differences in the conformational properties of the pyrrolidino rings in the σ-complexes and **5**. In **3** and **4a** the C atoms bonded to the Nα atoms are nearly coplanar with atoms C2–C6 (see Table VI for torsion angles). In **5**, the Cα′ atoms are displaced dramatically to the opposite side of the aromatic ring from the C_{Me} substituent, whereas the Cδ′ atoms are nearly coplanar with the Nα atoms and the aromatic ring. These conformational properties are illustrated in Figure 2. An analogous effect was noted in the 2,4,6-trinitro-2′,4′,6′-tripyrrolidinobiphenyl cited above, except that the disposition of the Cα′ atoms was to opposite sides of the phenyl ring to accommodate the 2,4,6-trinitrophenyl moiety. Interestingly, the Cα–Nα bonds are somewhat longer in the biphenyl (average 1.420 (0) Å) and the average Cβ–Cα–Nα–Cα′ torsion angle is greater as well (74.3 (1.8)°) compared with an average magnitude of 57.4 (7.5) for **5**. The sum of the bond angles around Nα for the biphenyl is 342.3°. These observations indicate that the distortions of the Nα atoms of the neutral molecules from sp^2 hybridization geometry result from steric effects.

In the σ-complexes, the more extensive through conjugation to the Nα atoms apparently prevents significant distortion of the binding geometry of the N atoms at the expense of increased nonplanarity in the conformation of the cyclohexadienylium ring of, e.g., **4a**. Thus the steric interactions between the *o*-pyrrolidino rings and bulky substituents at C1 and electronic interactions between Cα and Nα atoms contribute to the observed nonplanarity of **4a** and **6**.

The Theoretical Calculations. Simple perturbational considerations show and EH calculations confirm that on bending conformation **2B** to **2C** the two lowest filled p orbitals π_1 and π_2 of the pentadienylium moiety increase in energy and the empty orbital π_3, the LUMO of the σ-complex, decreases in energy.

Figure 3 presents the EH, MNDO, and 3-21G calculated energies[20] for several conformations of the cyclohexadienylium ion

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(20) All 3-21G energies and all MNDO energies and structures are the result of optimization in which the atoms Cα, Cαs, Cβ, Cβs, Cγ and the bonds Cβ–H, Cγ–H, Cβs–H were maintained in a plane. A mirror plane was assumed to pass through atoms C1 and Cγ.

Table III. Fractional Atomic Coordinates (with Estimated Standard Deviations) for Non-Hydrogen Atoms

3a

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cl	0.4126 (1)	0.244 (1)	0.2400 (2)	C22	0.0846 (5)	0.323 (3)	0.454 (1)
O1	0.4737 (4)	0.249 (3)	0.2853 (8)	C23	0.1323 (5)	0.250 (3)	0.3668 (7)
O2	0.388 (1)	0.392 (2)	0.271 (2)	C24	0.1973 (4)	0.248 (3)	0.4227 (6)
O3	0.4132 (6)	0.230 (5)	0.134 (1)	N4	0.3981 (3)	0.250 (2)	0.6588 (5)
O4	0.3745 (9)	0.116 (3)	0.283 (2)	C41	0.4244 (4)	0.248 (3)	0.5459 (7)
C1	0.2010 (3)	0.253 (3)	0.7334 (6)	C42	0.4941 (5)	0.289 (4)	0.570 (1)
C2	0.2257 (3)	0.243 (2)	0.6177 (5)	C43	0.5093 (4)	0.254 (4)	0.6737 (8)
C3	0.2904 (4)	0.244 (3)	0.5964 (6)	C44	0.4503 (4)	0.237 (4)	0.7422 (7)
C4	0.3356 (3)	0.241 (3)	0.6822 (6)	N6	0.2310 (3)	0.245 (2)	0.9239 (5)
C5	0.3161 (3)	0.252 (3)	0.7936 (6)	C61	0.2746 (4)	0.247 (2)	1.0182 (6)
C6	0.2521 (3)	0.245 (2)	0.8189 (6)	C62	0.2307 (4)	0.247 (3)	1.1162 (6)
N2	0.1807 (3)	0.241 (2)	0.5407 (5)	C63	0.1641 (5)	0.225 (4)	1.0765 (7)
C21	0.1108 (4)	0.247 (3)	0.5585 (6)	C64	0.1635 (3)	0.243 (3)	0.9537 (6)

3b

atom		*x*	*y*	*z*	atom		*x*	*y*	*z*
Br1	A	0.77281 (6)	0.77865 (6)	0.14482 (6)	C1	B	0.8886 (5)	0.4245 (5)	0.4277 (5)
Br1	B	0.70983 (6)	0.24955 (5)	0.31206 (5)	C2	B	0.8548 (5)	0.5123 (5)	0.3747 (5)
C1	A	0.5813 (5)	0.6128 (5)	0.0556 (5)	C3	B	0.9003 (5)	0.5499 (5)	0.3275 (4)
C2	A	0.6195 (5)	0.5231 (5)	0.1046 (4)	C4	B	0.9828 (5)	0.5072 (5)	0.3320 (4)
C3	A	0.5773 (5)	0.4790 (5)	0.1518 (5)	C5	B	1.0187 (5)	0.4237 (5)	0.3811 (5)
C4	A	0.4962 (5)	0.5184 (5)	0.1549 (4)	C6	B	0.9747 (5)	0.3826 (5)	0.4283 (5)
C5	A	0.4592 (5)	0.6061 (5)	0.1137 (5)	N2	B	0.7773 (5)	0.5496 (5)	0.3754 (4)
C6	A	0.4966 (5)	0.6502 (5)	0.0631 (4)	C21	B	0.7315 (6)	0.6343 (6)	0.3259 (5)
N2	A	0.6964 (4)	0.4902 (4)	0.1012 (4)	C22	B	0.6639 (6)	0.6607 (6)	0.3661 (6)
C21	A	0.7409 (5)	0.5297 (5)	0.0471 (5)	C23	B	0.6405 (6)	0.5668 (6)	0.3965 (6)
C22	A	0.8025 (6)	0.4487 (6)	0.0419 (5)	C24	B	0.7295 (6)	0.5106 (6)	0.4270 (5)
C23	A	0.8284 (5)	0.3969 (6)	0.1293 (5)	N4	B	1.0279 (4)	0.5460 (5)	0.2880 (4)
C24	A	0.7428 (5)	0.4043 (5)	0.1481 (5)	C41	B	1.0004 (5)	0.6345 (5)	0.2379 (5)
N4	A	0.4539 (4)	0.4718 (4)	0.1978 (4)	C42	B	1.0855 (6)	0.6609 (6)	0.2225 (5)
C41	A	0.4864 (5)	0.3812 (5)	0.2437 (5)	C43	B	1.1252 (6)	0.5650 (6)	0.2140 (6)
C42	A	0.4268 (6)	0.3682 (6)	0.2940 (6)	C44	B	1.1119 (5)	0.5055 (5)	0.2841 (5)
C43	A	0.3362 (6)	0.4149 (7)	0.2349 (6)	N6	B	1.0040 (4)	0.3037 (4)	0.4754 (4)
C44	A	0.3671 (5)	0.5026 (5)	0.2023 (5)	C61	B	1.0875 (5)	0.2535 (5)	0.4826 (5)
N6	A	0.4605 (4)	0.7292 (4)	0.0174 (4)	C62	B	1.0814 (6)	0.1597 (6)	0.5248 (5)
C61	A	0.3767 (6)	0.7749 (5)	0.0153 (5)	C63	B	1.0305 (6)	0.1863 (6)	0.5831 (5)
C62	A	0.3515 (6)	0.8457 (6)	−0.0603 (5)	C64	B	0.9601 (6)	0.2587 (5)	0.5279 (5)
C63	A	0.4458 (6)	0.8726 (6)	−0.0575 (5)					
C64	A	0.4990 (6)	0.7801 (6)	−0.0366 (5)					

4a

atom		*x*	*y*	*z*	atom		*x*	*y*	*z*
Cl1		0.35081 (4)	0.05963 (2)	0.19939 (2)	C22		−0.2065 (2)	0.2616 (1)	0.72096 (8)
O1		0.2454 (1)	−0.01080 (9)	0.16032 (8)	C23		−0.3534 (2)	0.2062 (1)	0.68594 (9)
O2		0.4969 (1)	0.06043 (9)	0.16292 (7)	C24		−0.3044 (2)	0.16083 (9)	0.60953 (8)
O3		0.2771 (1)	0.15316 (8)	0.19027 (7)	N4		−0.0969 (1)	0.02748 (8)	0.36137 (6)
O4		0.3826 (2)	0.03739 (8)	0.28384 (7)	C41		−0.2331 (2)	−0.0351 (1)	0.37187 (8)
C	Me	−0.0509 (2)	0.3602 (1)	0.46566 (9)	C42		−0.2227 (2)	−0.1124 (1)	0.30822 (9)
C1		0.0321 (1)	0.26947 (8)	0.50390 (7)	C43		−0.1506 (2)	−0.0594 (1)	0.24103 (8)
C2		−0.0947 (1)	0.20008 (9)	0.52453 (7)	C44		−0.0252 (2)	0.00378 (9)	0.28753 (8)
C3		−0.1356 (2)	0.12211 (9)	0.47631 (8)	N6		0.2752 (1)	0.27482 (8)	0.43828 (6)
C4		−0.0474 (1)	0.09925 (8)	0.41103 (7)	C61		0.3854 (2)	0.24079 (9)	0.38248 (8)
C5		0.0931 (1)	0.14970 (9)	0.39901 (7)	C62		0.5162 (2)	0.3161 (1)	0.38853 (9)
C6		0.1387 (1)	0.22888 (8)	0.44586 (7)	C63		0.5134 (2)	0.3588 (1)	0.47244 (8)
N2		−0.1728 (1)	0.22077 (8)	0.58811 (6)	C64		0.3373 (2)	0.3605 (1)	0.4824 (1)
C21		−0.1394 (2)	0.2993 (1)	0.64630 (8)					

5

atom		*x*	*y*	*z*	atom		*x*	*y*	*z*
C1		0.2869 (1)	0.3748 (1)	0.11356 (6)	C24		0.0253 (1)	0.2702 (2)	−0.01068 (6)
C2		0.22185 (9)	0.3082 (1)	0.05465 (6)	N4		0.46787 (8)	0.2018 (1)	−0.06426 (5)
C3		0.28097 (9)	0.2482 (2)	−0.00424 (6)	C41		0.4088 (1)	0.1271 (2)	−0.12603 (6)
C4		0.40823 (9)	0.2541 (1)	−0.00597 (5)	C42		0.5103 (1)	0.1229 (2)	−0.17896 (6)
C5		0.4738 (1)	0.3125 (1)	0.05355 (6)	C43		0.6238 (1)	0.0906 (2)	−0.13243 (6)
C6		0.41478 (9)	0.3669 (1)	0.11337 (5)	C44		0.5999 (1)	0.1878 (2)	−0.06468 (6)
C1	Me	0.2227 (1)	0.4726 (2)	0.16924 (7)	N6		0.48389 (9)	0.4215 (1)	0.17291 (5)
N2		0.09317 (8)	0.3097 (1)	0.05485 (5)	C61		0.6164 (1)	0.4245 (2)	0.16830 (6)
C21		0.0358 (1)	0.2058 (2)	0.10834 (7)	C62		0.6596 (1)	0.4544 (2)	0.24422 (7)
C22		−0.0993 (1)	0.2321 (2)	0.09137 (8)	C63		0.5755 (1)	0.3375 (2)	0.28355 (6)
C23		−0.1067 (1)	0.2626 (2)	0.01135 (8)	C64		0.4534 (1)	0.3594 (2)	0.24369 (6)

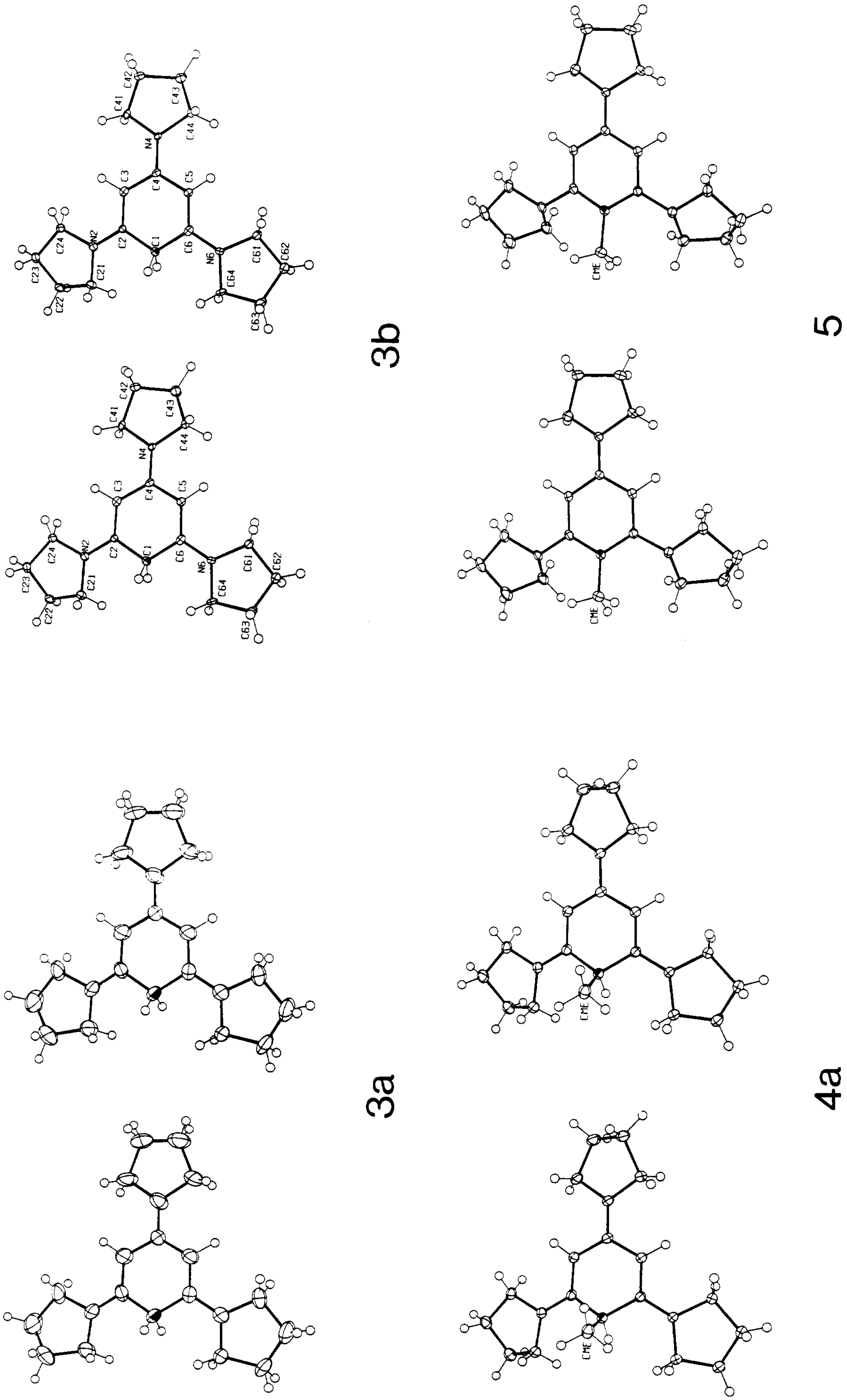

Figure 1. Stereoscopic projections[15] illustrating the conformations of **3a**, one molecule of **3b**, **4a**, and **5**. The atom labeling scheme is illustrated for **3b**.

Table IV. Selected Bond Distances (Å) with Estimated Standard Deviations

		3b			
	3a	A	B	**4a**	**5**
C1–CMe				1.556 (2)	1.508 (2)
C1–C2	1.512 (10)	1.498 (10)	1.493 (10)	1.518 (2)	1.411 (2)
C6–C1	1.499 (10)	1.505 (13)	1.493 (12)	1.510 (2)	1.413 (2)
C2–C3	1.376 (10)	1.382 (13)	1.383 (13)	1.379 (2)	1.398 (2)
C5–C6	1.372 (10)	1.372 (13)	1.384 (13)	1.388 (2)	1.398 (2)
C3–C4	1.414 (10)	1.430 (12)	1.422 (12)	1.428 (2)	1.407 (1)
C4–C5	1.428 (11)	1.426 (10)	1.418 (10)	1.420 (2)	1.400 (2)
C2–N2	1.332 (9)	1.337 (12)	1.349 (12)	1.346 (2)	1.402 (1)
C6–N6	1.362 (9)	1.343 (9)	1.336 (9)	1.344 (2)	1.410 (2)
C4–N4	1.337 (9)	1.346 (12)	1.342 (12)	1.342 (2)	1.372 (2)
N2–C21	1.476 (10)	1.473 (13)	1.475 (13)	1.476 (2)	1.470 (2)
N2–C24	1.490 (10)	1.470 (10)	1.470 (10)	1.473 (2)	1.464 (2)
N4–C41	1.490 (11)	1.477 (9)	1.472 (19)	1.476 (2)	1.449 (2)
N4–C44	1.498 (11)	1.482 (12)	1.484 (12)	1.476 (2)	1.468 (2)
N6–C61	1.471 (10)	1.473 (12)	1.470 (11)	1.472 (2)	1.468 (2)
N6–C62	1.455 (9)	1.475 (13)	1.476 (12)	1.475 (2)	1.482 (2)
C21–C22	1.517 (17)	1.539 (12)	1.520 (12)	1.524 (2)	1.528 (2)
C22–C23	1.562 (18)	1.527 (12)	1.527 (13)	1.530 (2)	1.538 (2)
C23–C24	1.521 (13)	1.527 (13)	1.535 (15)	1.527 (2)	1.531 (2)
C41–C42	1.515 (15)	1.518 (15)	1.529 (14)	1.528 (2)	1.531 (2)
C42–C43	1.342 (18)	1.520 (12)	1.533 (12)	1.531 (2)	1.530 (2)
C43–C44	1.497 (13)	1.522 (14)	1.526 (14)	1.530 (2)	1.531 (2)
C61–C62	1.511 (11)	1.529 (11)	1.529 (12)	1.526 (2)	1.521 (2)
C62–C63	1.484 (14)	1.534 (14)	1.553 (15)	1.530 (2)	1.526 (2)
C63–C64	1.513 (11)	1.523 (12)	1.517 (11)	1.523 (2)	1.532 (2)

Table V. Selected Bond Angles (deg) with Estimted Standard Deviations

		3b			
	3a	A	B	**4a**	**5**
C2–C1–C_{Me}				108.4 (1)	120.7 (1)
C6–C1–C_{Me}				108.6 (1)	121.2 (1)
C2–C1–C6	114.3 (6)	115.4 (7)	116.1 (8)	113.4 (1)	117.5 (1)
C1–C2–C3	120.9 (6)	120.9 (7)	121.0 (8)	120.8 (1)	121.6 (1)
C1–C6–C5	122.2 (7)	121.8 (7)	120.8 (6)	121.0 (1)	120.6 (1)
C2–C3–C4	120.9 (6)	120.4 (6)	120.0 (7)	120.4 (1)	120.1 (1)
C6–C5–C4	119.5 (7)	119.8 (8)	120.2 (8)	120.2 (1)	121.1 (1)
C3–C4–C5	121.4 (6)	121.5 (8)	121.9 (8)	121.1 (1)	118.7 (1)
C1–C2–N2	115.2 (6)	116.5 (7)	115.3 (8)	117.8 (1)	118.4 (1)
C1–C6–N6	115.6 (7)	115.8 (8)	115.7 (8)	117.7 (1)	119.8 (1)
C3–C2–N2	123.9 (6)	122.6 (6)	123.7 (7)	121.3 (1)	120.0 (1)
C5–C6–N6	121.9 (7)	122.5 (8)	123.5 (8)	121.2 (1)	119.5 (1)
C3–C4–N4	119.3 (7)	119.3 (6)	119.4 (6)	119.2 (1)	121.1 (1)
C5–C4–N4	118.8 (7)	119.2 (8)	118.7 (8)	119.7 (1)	120.2 (1)
C2–N2–C21	126.3 (6)	125.3 (6)	123.8 (6)	127.4 (1)	116.9 (1)
C6–N6–C64	123.4 (6)	124.5 (8)	125.1 (7)	127.3 (1)	119.4 (1)
C2–N2–C24	121.6 (6)	122.3 (7)	123.9 (8)	121.5 (1)	118.5 (1)
C6–N6–C61	123.0 (6)	123.4 (8)	122.5 (7)	121.3 (1)	118.0 (1)
C21–N2–C24	111.9 (6)	112.2 (2)	112.2 (7)	111.0 (1)	104.3 (1)
C61–N6–C64	113.6 (6)	112.0 (6)	112.4 (6)	111.3 (1)	108.5 (1)
C4–N4–C41	124.0 (6)	123.9 (7)	124.2 (7)	124.5 (1)	124.2 (1)
C4–N4–C44	123.9 (7)	124.7 (6)	124.4 (6)	123.9 (1)	122.3 (1)
C41–N4–C44	111.5 (6)	111.3 (7)	111.4 (4)	111.6 (1)	112.6 (1)

2a (R = R′ = H). Even when one is skeptical about the numerical reliability, the results show that the energy required for bending the benzenium ring is comparatively small. **2a** is certainly not a rigid planar system of conformation **2B**, but rather, the saturated C atom can easily swing through the plane of this energetically stable conformation (see Scheme II). These results are in concurrence with CNDO calculations for **2b** (R = H, R′ = CH_3) in conformation **2C** reported earlier.[21] For highly substituted σ-complexes a bent conformation (**2A**, **2C**) was found in solution.[22]

A priori, the low energy required to bend the stable conformation from planarity should be reduced even further by (partially) populating the LUMO π_3 orbital which is energetically stabilized by bending the conformation. Such population can occur by reduction of the σ-complex to a neutral radical, to a negative Meisenheimer complex, by the presence of π-electron donors in positions α and/or γ with a large density coefficient for the nonbonding pentadienyl orbital, and/or by hyperconjugation interaction between π_3 (as the acceptor) and the C1 RR′ group (the donor).

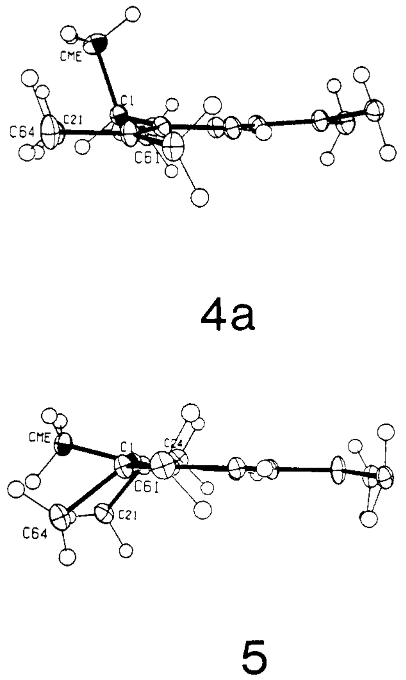

Figure 2. An illustration of the conformational differences between σ-complex **4a** and it's parent **5**. A portion of the pyrrolidino rings has been deleted for clarity. Note the positions of the C1-methyl groups and the pyrrolidino Cα′ and Cδ′ atoms.

Going from planar conformation **2B** to nonplanar conformation **2C** results in increasing overlap between the LUMO π_3 orbital and the C1–R′ bond (which becomes quasiaxial), whereas the overlap between π_3 and C1–R (which becomes quasiequatorial) is decreased. That is, the hyperconjugation between the π_3 orbital (a potential acceptor orbital) and the σ_A orbital (a potential donor

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(21) Heidrich, D.; Grimmer, M.; Sommer, B. *Tetrahedron* **1976**, *32*, 2027–2032.

(22) (a) Olah, G. A.; Spear, R. J.; Messina, G.; Westerman, P. W. *J. Am. Chem. Soc.* **1975**, *97*, 4051–4055. (b) Brouwer, D. M.; Mackor, E. L.; MacLean, C. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 1564–1598. (c) Mackor, E. L.; MacLean, C. *Pure Appl Chem.* **1964**, *8*, 393–404.

Table VI. Selected Torsion Angles (deg) with Estimated Standard Deviations

	3a	3b		4a	5
		A	B		
C1–C2–C3–C4	4.5 (29)	−0.1 (7)	−0.3 (10)	7.0 (2)	−0.3 (2)
C1–C6–C5–C4	−5.9 (27)	−5.2 (10)	0.7 (10)	−6.7 (2)	−4.2 (2)
C2–C3–C4–C5	−5.3 (31)	−3.3 (10)	2.7 (10)	6.5 (2)	3.4 (2)
C3–C4–C5–C6	7.9 (30)	6.0 (9)	−1.7 (10)	−6.6 (2)	−1.1 (2)
C3–C2–C1–C6	−9.9 (30)	0.8 (9)	1.6 (9)	−18.6 (2)	−4.8 (2)
C5–C6–C1–C2	8.8 (30)	1.8 (9)	−0.7 (9)	18.5 (2)	7.1 (2)
C1–C2–N2–C21	−0.3 (22)	−6.0 (9)	2.3 (9)	6.5 (2)	−64.9 (1)
C1–C6–N6–C64	3.5 (26)	−1.0 (9)	−2.3 (9)	1.9 (2)	49.6 (1)
C3–C2–N2–C24	−2.9 (29)	−0.3 (9)	0.4 (9)	0.5 (2)	−8.4 (2)
C5–C6–N6–C61	−2.0 (29)	−1.5 (10)	1.1 (10)	−2.6 (2)	2.2 (1)
C3–C4–N4–C41	−5.2 (30)	0.6 (9)	3.5 (10)	−4.0 (2)	−4.1 (2)
C5–C4–N4–C44	12.1 (29)	3.3 (9)	2.3 (10)	−7.8 (2)	6.4 (2)

Table VII. Selected Average Bonding Parameters[a]

	3	4a	5
	Bond Distances		
C1–Cα	1.500 (7)	1.514 (4)	1.412 (1)
Cα–Cβ	1.378 (5)	1.383 (5)	1.398 (0)
Cβ–Cγ	1.423 (6)	1.424 (4)	1.404 (4)
Cα–Nα	1.343 (10)	1.345 (1)	1.406 (4)
Cγ–Nγ	1.342 (4)	1.342	1.372
N–C_{pyr}	1.476 (9)	1.475 (2)	1.467 (10)
C_{pyr}–C_{pyr}	1.507 (62)	1.528 (3)	1.530 (4)
	Bond Angles		
Cα–C1–C_{Me}		108.5 (1)	121.0 (2)
Cα–C1–Cα†	115.3 (7)	113.4	117.5
C1–Cα–Cβ	121.3 (5)	120.9 (1)	121.1 (5)
Cα–Cβ–Cγ	120.1 (4)	120.3 (1)	120.6 (5)
Cβ–Cγ–Cβ†	121.6 (3)	121.1 (1)	118.7 (1)
C1–Cα–Nα	115.7 (4)	117.8 (1)	119.1 (7)
Cβ–Cα–Nα	123.0 (7)	121.2 (1)	119.8 (2)
Cβ–Cγ–Nγ	119.1 (3)	119.4 (2)	120.4 (4)
Cα–Nα–Cα′	124.7 (10)	127.3 (1)	118.2 (12)
Cα–Nα–Cδ′	122.8 (8)	121.4 (1)	118.2 (2)
Cα′–Nα–Cδ′	112.4 (6)	111.2 (3)	106.4 (21)
Cγ–Nγ–Cα″	124.2 (3)	124.2 (3)	123.2 (10)
Cα″–Nγ–Cα″†	111.4 (1)	111.6	112.6

[a] The atom labeling is depicted in Scheme IV. The symbol (†) is used to designate atoms related by C_s symmetry that are involved in the tabulated angles. The subscript (pyr) indicates that all examples of the specified parameter of the pyrrolidino rings have been included in the averages. Numbers in parentheses are standard deviations from the average values; they reflect experimental consistancy rather than precision. Where no indication of a deviation is given the parameter is single valued.

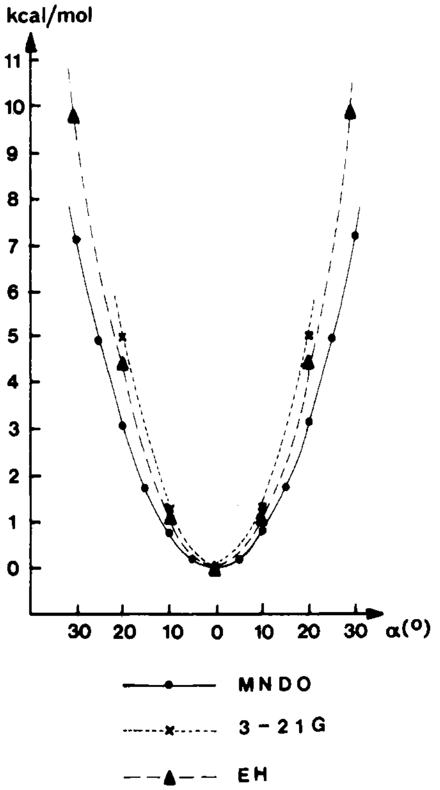


Figure 3. EH, MNDO, and 3-21G results for the energy of conformation **2A–C**; for **2a** (R = R′ = H), the MNDO and 3-21G energies are for the fully optimized structures.

orbital) increases while that between the π_3 and σ_E orbitals decreases (Figure 4). Thus in the nonplanar conformation the σ_A bond is weakened and the σ_E bond is strengthened due to hyperconjugation. Consequently, while the C–R and C–R′ bonds are a priori equivalent in planar conformation **2B**, in the nonplanar conformations equatorial and axial bonds with markedly different hyperconjugation must differ in their reaction properties.

MNDO calculations for a series of angles α in the range 0 to 40° for σ-complexes **2a** and **2b** show that the σ_A bond length has a maximum at α = 25° in **2a** and at 23° in **2b**. Taking the value of the σ_A bond length as a measure of the degree of hyperconjugation indicates that the hyperconjugation effect is maximal in the range 23–25°. An analogous EH calculation for **2a** shows that the reduced Mulliken's overlap population for the axial bond has a minimum at α = 25°, which reflects good numerical consistency with the MNDO results.

The hyperconjugation in the nonplanar conformation (see Figure 4) increases as (a) the energy level of the LUMO π_3 decreases, (b) the energy level of the donor orbital, σ_A, increases, and (c) the amount of overlap between π_3 and σ_A increases (i.e., the MO coefficient of σ_A for atom C1 increases).

Standard perturbation theory considerations provide a rule of thumb that the energy level of the σ-orbital of a C–R′ bond will be higher and the LCAO coefficient for the C atom will be larger (a) the more electropositive the ligand R′ is and (b) the longer the C–R′ bond is. Consequently, the σ-orbital of a long C–R′ bond to an electropositive ligand R′ has optimal donor properties for hyperconjugation with the π_3 orbital. The reciprocal is true by analogy.

For σ-complexes with identical ligands, the most stable conformation, at least electronically, is the planar one, due to (a) the π-system, which favors the planar structure, and (b) the stabilizing hyperconjugation, which is at a maximum in the planar conformation for the CRR′ group with R = R′.

With different ligands, R ≠ R′, conformations **2A** and **2C** are not of equal energy and the conformation for which the ligand with the better donor σ-orbital is axial is the more stable. Considering purely hyperconjugation effects, the energy difference between the two conformations is directly related to the difference in the donor properties of the C–R and C–R′ bonds.

Provided that the potential energy variation is harmonic in the area of the minimum and that the function is influenced only by hyperconjugation effects, one expects the energy minimum to be shifted from the planar conformation **2B** in the direction of the more stable conformation **2A** or **2C**.

Considering steric as well as hyperconjugation effects, if the better donor bond is the σ-bond to the ligand R′ with the greater steric requirement, one expects the steric and electronic effects

Table VIII. Relative MNDO Energies for Different Conformations of Selected σ-Complexes (Cyclohexadienylium Ions) **2**[a]

compd	R′	R	α_s[c]	$E(\alpha)$[b] 20°	0°	−20°	ΔE[d]
2a	H	H	0.1	3.10	0.00	3.10	0.00
2b	CH_3	H	0.5	3.06	0.00	3.22	0.16
2c	*t*-Bu	H	1.9	2.86	0.03	3.46	0.60
2d	H	F	8.3	1.46	0.47	5.13	3.67
2e	H	Cl	0.0	2.79	0.00	3.11	0.32
2f	Br	H	1.9	2.78	0.04	3.60	0.82
2g	I	H	4.4	2.39	0.18	5.03	2.64
2h	H	OH	4.4	1.73	0.13	3.84	2.11
2i	SH	H	2.2	2.56	0.04	3.68	1.12
2j	H	CF_3	1.0	2.66	0.03	3.48	0.82
2k	$2e^-$[e]	H	17.3	0.13	4.45	20.36	20.23
2l	$2e^-$	CH_3	17.1	0.09	4.25	19.96	19.87
2m	Cl	F	6.2	1.70	0.33	5.22	3.52
2n	CH_3	CH_3	0.0	3.70	0.00	3.70	0.00
2o	CH_3	F	7.4	1.35	0.37	4.92	3.57
2p	CH_3	Cl	0.0	3.07	0.00	3.36	0.29
2q	Br	CH_3	1.3	3.19	0.01	3.84	0.65
2r	I	CH_3	2.9	3.05	0.09	5.07	2.02
2s	H	NO_2[f]	2.3	2.33	0.04	3.54	1.21
2t	SO_3H	H	2.1	2.91	0.04	3.84	0.93
2u	I	F	8.0	1.54	0.64	7.17	5.63
2v	Ph[f]	H	1.1	2.92	0.01	4.01	1.09

[a] Energies (kcal/mol) are given relative to that of the most stable conformer of each compound. A positive angle α corresponds to a conformer with R′ quasiaxial; $\alpha = 0$ corresponds to the planar conformation. [b] Relative energies calculated[20] for the indicated α values. [c] The α value (deg) for the most stable conformation. [d] The energy difference between the two nonplanar conformers ($\alpha = \pm 20°$). [e] An electron pair. The sp^3 hybridization of atom C1 was maintained through the optimization. [f] The indicated substituent was maintained in the mirror symmetry plane of the σ-complex.

Table IX. Relative MNDO Energies for Different Conformations of Selected σ-Complexes **8** and **9**[a]

compd	R′	R	α_s	$E(\alpha)$ 20°	0°	−20°	ΔE
8a	H	H	0.1	1.66	0.00	1.66	0.00
8b	CH_3	H	21.6	0.03	3.98	12.38	12.35
8c	Et	H	20.2	0.00	3.64	12.29	12.29
8d	*i*-Pr	H	34.6	3.12	3.66	14.78	11.60
8e	*t*-Bu	H	32.1	2.13	13.07	27.61	25.48
8f	CH_3	CH_3	1.5	2.80	0.04	2.80	0.00
8g	H	F	0.1	0.92	0.00	2.41	1.49
8h	Cl	H	13.5	0.23	1.45	7.71	7.48
8i	Br	H	15.5	0.17	1.87	8.87	8.60
8j	I	H	18.7	0.02	2.95	11.34	11.32
8k	OCH_3	H	9.5	0.84	0.64	6.02	5.18
9a	CH_3	CH_3	0.0	3.65	0.00	3.65	0.00
9b	CH_3	Ph[b]	4.1	5.84	0.36	12.17	6.33

[a] For definitions of symbols and description of entries see Table VIII. [b] The phenyl ring is rotated 0.7° out of the mirror symmetry plane of the σ-complex.

to be additive and the nonplanar conformation with this ligand in the quasiaxial position (the position of the weakened bond) to be more stable. If the smaller ligand is the one for which the σ-bond has the better donor properties, the effects compete, which would lead to a smaller deviation from planarity and less bond weakening.

Table VIII displays MNDO results for a large number of σ-complexes **2** unsubstituted in the pentadienyl moiety and with ligands R and R′ of different steric and electronic character. The results show that, for these σ-complexes, the steric influence of the ligands at C1 is very small; e.g., for **2c**, a compound with substituents with very different steric requirements, the calculated nonplanarity is only $\alpha = 1.9°$. Because of the minimal influence of the steric effects, the hyperconjugation effects dominate for the compounds **2d**, **2h**, **2j**, and **2s**, which results in the smaller but better donor ligand being in the quasiaxial position. In the other compounds calculated to be significantly nonplanar, the steric and electronic effects are additive.

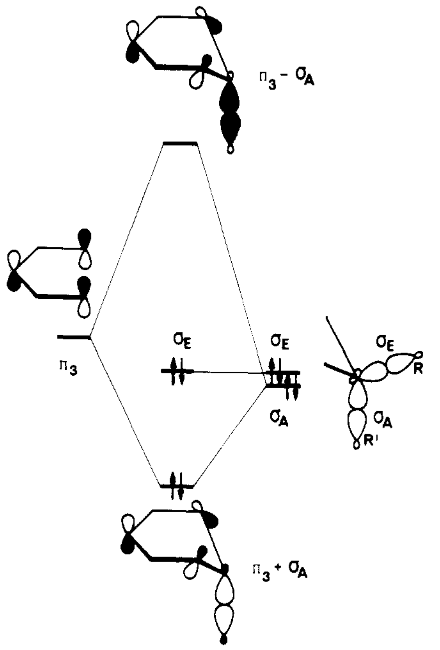
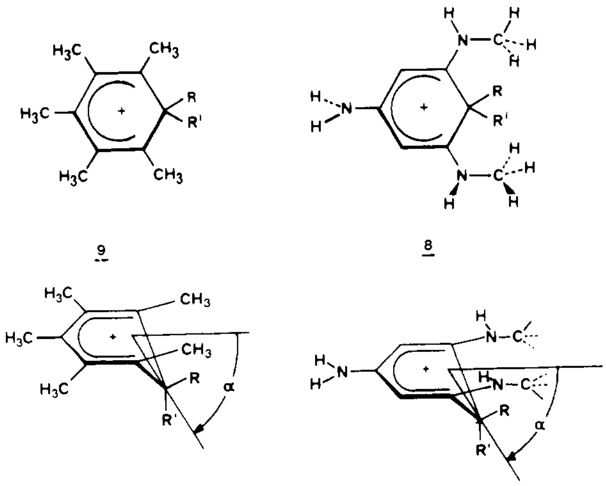
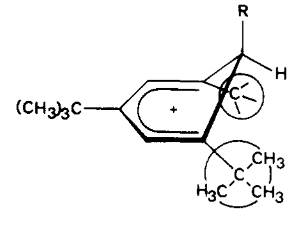


Figure 4. Hyperconjugation between the π_3 orbital of the pentadienylium moiety (left) and the σ_A orbital (right) of the axial bond –C–R′; the σ_E orbital of the –C–R bond displays practically no overlap with the π system and consequently no hyperconjugation.

Scheme V

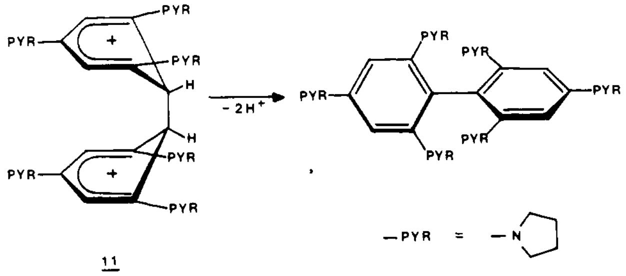


Scheme VI



10

Scheme VII



11

Table X. A Comparison of Bonding Geometries Obtained from MNDO Calculations and X-ray Crystal Structure Determinations

compd	α	C1–Cα	Cα–Cβ	Cβ–Cγ	C1–R′	C1–R	Cα–Rα′	Cγ–Rγ′
8a (MNDO)	0.1	1.525	1.396	1.439	1.117	1.117	1.367	1.354
3a (X-ray)	6.3							
3b (X-ray) (A)[a]	0.8	1.500	1.378	1.423			1.343	1.342
3b (X-ray) (B)	1.0							
8b (MNDO)	21.6	1.537	1.400	1.438	1.559	1.116	1.369	1.355
4a (X-ray)	15.4	1.514	1.383	1.424	1.561		1.345	1.342
8c (MNDO)	15.5	1.527	1.397	1.440	1.895	1.111	1.368	1.353
6 (X-ray)	15.0	1.491	1.366	1.433	2.000		1.345	1.364
9a (MNDO)	0.1	1.526	1.400	1.452	1.578	1.581	1.521	1.532
7a (X-ray)	5.4	1.490	1.365	1.407	1.538	1.586	1.490	1.501
9b (MNDO)	4.1	1.532	1.403	1.448	1.578	1.557	1.512	1.530
7b (X-ray)	7.6	1.498	1.368	1.416	1.571	1.577	1.487	1.497

[a] The bend angles, α, are listed separately for the three independent observations. Bond distances have been averaged.

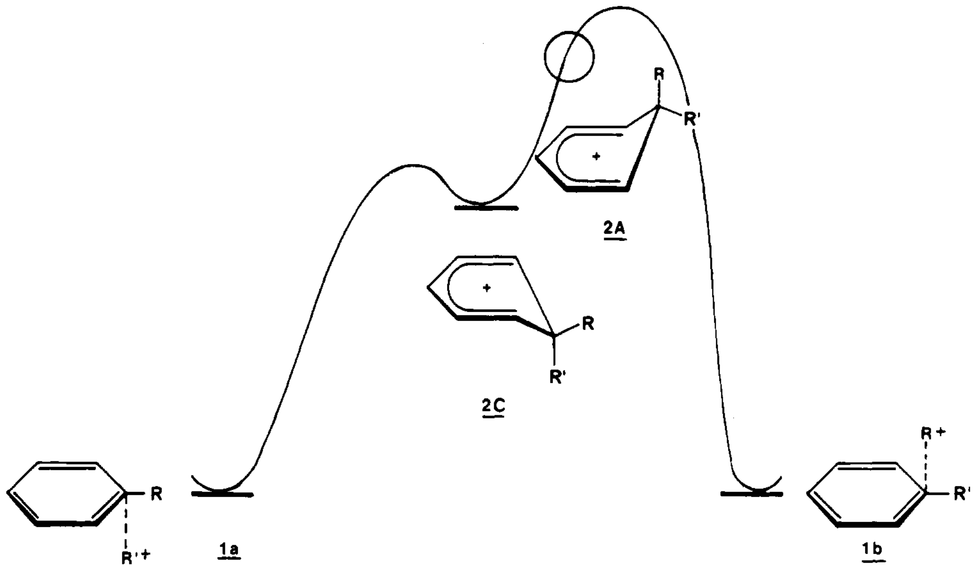
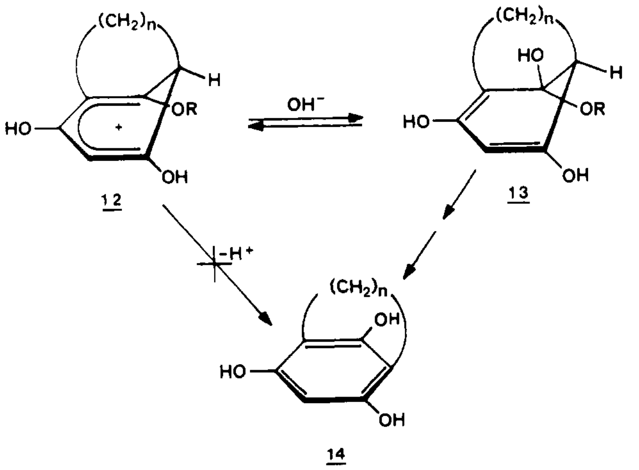


Figure 5. A simplified energy hypersurface of the electrophilic substitution on aromatics with nonplanar intermediate σ-complexes.

Scheme VIII



Except for **2k** and **2l**, which contain extremely good donor "ligands", the calculated deviations from planarity are far smaller than the 20 to 25° necessary for the maximum hyperconjugative weakening of the axial bond. However, for the nonplanar σ-complexes, as well as for the planar ones with R $\neq$ R′, considerably less energy is necessary to bring the ligand R′ into the quasiaxial position of a conformer with $\alpha = 20°$ than is needed to bring ligand R into this position, which means that, due to stereoelectronic effects, the C–R′ bond is predestined for cleavage.

Comparison of Crystallographic and Theoretical Results. To examine the validity of the MNDO calculations, structures **8** and **9** (Scheme V), with different R and R′ ligands were optimized with MNDO methods and compared with the results from the X-ray crystal structure determinations described above. Analogous to **3** and **4a**, the two *N*-methyl groups in series **8** were held constant with the N–H and a C–H bond in a syn-planar conformation. The MNDO results are presented in Table IX; Table X compares the results from the crystal structure determinations. Examination of the tables demonstrates that the MNDO results are in reasonable agreement with the experimental data.

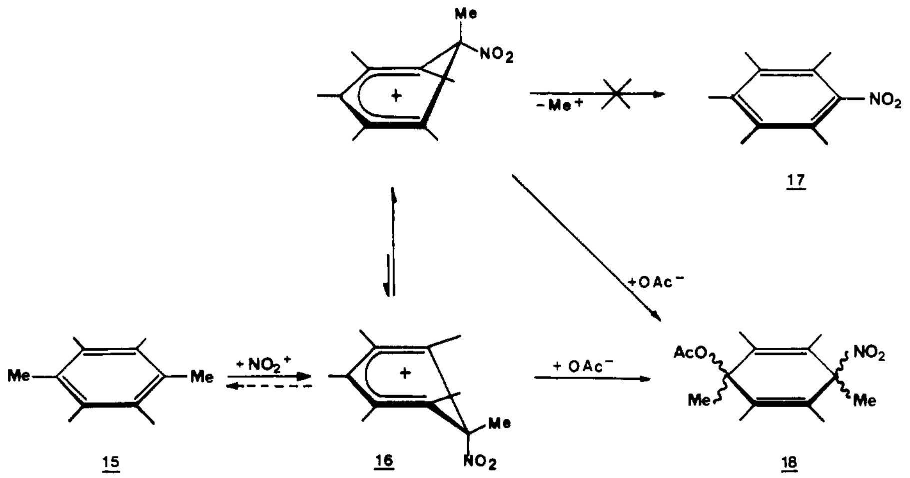
In particular, the MNDO results confirm that (a) the planar conformation is the stable one for σ-complexes with identical ligands R and R′ (based on the above considerations and the MNDO results, we believe that the angle $\alpha = 5.4°$ in complex **7a** is the result of packing effects) and (b) a nonplanar conformation is stable in the case of different ligands, R $\neq$ R′ (Table IX, except for **8g** with R′ = F and R = H), and that the deviations from planarity are much more pronounced in the examples of Table IX than in those of Table VIII.

The large increase in the deviation from planarity resulting from introduction of donor substituents (Table VIII–IX) can be explained easily in terms of two competing effects, one a hyperconjugation effect and the other a population of the π_3 orbital.

The R $\neq$ R′ complexes in the absence of donors the hyperconjugation effect yields only a small deviation from planarity (Table VIII). The effect is reduced by the introduction of donor substituents which results in even more of an increase in the energy of the LUMO π_3. Consequently the deviation from planarity due to hyperconjugation effects is reduced by the presence of donor substituents. For **2d** the angle of deviation $\alpha = 8.3°$ is reduced to 5.5° by the introduction of a NH_2 group in the γ position.[23]

The partial population of the π_3 orbital by the introduction of

Scheme IX



donor substituents, in contrast, decreases the energy necessary to achieve nonplanar conformations. Therefore a given, fixed steric hindrance between ligands in the ortho,ortho′ positions and the CRR′ group results in a larger deviation from planarity in the presence compared to that in the absence of donors.

Thus the steric effect of donor substituents in the ortho,ortho′ positions is reinforced by the electronic effects caused by these substituents. The steric and electronic effects would be competitive for acceptor substituents.

The same reasons provide the explanation for the large energy differences between the stable conformation with the R′ ligand in the quasiaxial position (i.e., $\alpha = +20°$, Table IX) and the inverted conformation with R quasiaxial ($\alpha = -20°$).

These observations not only illustrate the strong steric influence of the ortho,ortho′ donors, reinforced by their electronic effects, but also indicate that the population of the inverted conformations is likely to be very small compared to the more stable one.

Compound **8g** provides an interesting example of the interaction of the steric and electronic effects in determining conformation. The stable conformation is planar. Obviously, in contrast to **2d**, the steric effects (F favored in the quasiaxial position) and the hyperconjugation effects (F favored quasiequatorial) cancel each other.

In the case of the planar σ-complexes in Table IX with R = R′, the MNDO-calculated energy necessary to cause nonplanarity with $\alpha = 20°$ is considerably less than for the examples in Table VIII. For example, when going from **2a** to **8a** this energy is reduced from 3.1 to 1.66 kcal/mol; going from **2n** to **8f** the reduction is from 3.7 to 2.8 kcal/mol. These substantial reductions in distortion energy are, again, the result of steric effects, which are reinforced by electronic contributions.

In the case of planar **8g**, with R′ = H and R = F, the two conformations, $\alpha = \pm 20°$, also differ energetically, however, only by 1.49 kcal/mol. The conformation with $\alpha = 20°$, i.e., the H atom in the axial position, is the more stable one. Obviously, as in the case of **2d**, these conformations are determined predominantly by hyperconjugative effects, however, to a smaller extent than in **2d** where the corresponding differences in energy of the two conformations is 3.67 kcal/mol.

Reactivity of the σ-Complexes as a Function of Their Conformation

Considering the theoretical and experimental results presented thus far, the influence of conformation on the reaction properties of the intermediate σ-complexes can be described by two limiting cases LI and LII. **LI**: The most stable conformation for the σ-complex is a nonplanar one with a potential leaving ligand R′ in the axial position, **2C**. **LII**: The most stable conformation is a nonplanar one with the potential leaving ligand R′ in the equatorial position, **2A**.

The rearomatization, by elimination of R'^{+} is favored kinetically from stereoelectronic considerations for case LI compared to case LII because in the latter case dissociation requires adoption of an energetically unfavorable conformation close to **2C** with R′ in a quasiaxial position. Figure 5 illustrates this concept graphically. For case **2C** in which the stable conformation has an axial R′ ligand and an equatorial R ligand, the rearomatization to **1a** is favored over that to **1b** which would require the reaction to procede through a high-energy conformation close to **2A**.

These results are relevant to electrophilic substitution of aromatics. Under otherwise constant conditions, it follows that if the entering group for the formation of the intermediate σ-complex prefers the axial position the second energy barrier (reaction from left to right in Figure 5) is responsible for the rate-determining step. In the reciprocal case, when the entering group prefers the equatorial position and the leaving group is axial, the first activation energy barrier is rate determining (reaction from right to left in Figure 5).

To summarize, the above results concerning the factors that determine conformation allow the formulation of the following rules of thumb:

(a) For aromatics with small groups in the ortho,ortho′ positions relative to the substitution site, electronic effects govern the kinetics (i.e., the first reaction barrier is rate determining for strong electronegative entering and/or strong electropositive leaving groups, and vice versa).

(b) For aromatics with bulky substituents in the ortho,ortho′ positions, the second reaction barrier is rate determining if the entering group has large and/or the leaving groups small steric requirements, and vice versa.

These results indicate that in addition to the well-known electronic stabilization, the possibility of purely steric stabilization of a σ-complex, with respect to rearomatization, by bulky substituents in ortho and ortho′ positions also exists. In the case of a nonplanar σ-complex whose axial ligand displays no tendency to dissociate, the thermodynamic dissociation tendency of the equatorial ligand has no influence on the reaction as long as the energy necessary to invert the σ-complex to the other nonplanar conformation is large. A possible example is the (1*R*)-2,4,6-tri-*tert*-butylcyclohexadienylium σ-complex **10** with a poor leaving group R (Scheme VI).

The concepts that we have presented here provide explanations for experimental results that were previously very difficult to understand; three examples illustrate this phenomenum:

Example 1: Planar σ-complex **3** has a pK_a value of 9.6;[24] in contrast, the values for nonplanar **4** are markedly higher (13.3,

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(23) These values result from MNDO calculations analogous to those in Tables VIII and IX.

(24) (a) Schoeller, W. W. Thesis, Universität Stuttgart, 1969. (b) Vogel, S.; Knoche, W.; Schoeller, W. W. *J. Chem. Soc., Perkin Trans. 2* **1986**, 769–772.

14.3, 14.7, and 15.0, respectively).[24a] These large differences cannot be explained by purely electronic considerations; however, consideration of steric effects allows for an easily understood explanation. The energy necessary for the conversion of planar **3** to a nonplanar conformation ($\alpha = 20°$) with a quasiaxial C–H bond is small (1.66 kcal/mol for model compound **8a**). In contrast, as Table IX shows, the energy necessary to convert the nonplanar, nonacidic, σ-complexes (with an equatorial C–H bond) into the conformation necessary for proton dissociation (the inverted conformation with a quasiaxial C–H bond) is considerable. Which means that there is a very low population of conformers with the "acidic" inverted conformation compared to those with the stable "nonacidic" conformation, or at the macroscopic level, the equilibrium situation is described by a high pK_a value. For the same reason, proton dissociation from the dimeric σ-complex (Scheme VII), **11**, is extremely difficult[25] (for the structure of **11**, see ref 8a).

Example 2: In the phloroglucinophane σ-complexes (Scheme VIII), the bridged structure fixes the alkyl substituent in the axial position and the H atom in the equatorial position. Although thermodynamically favorable, direct deprotonation of the equatorial protons in **12** is so strongly hindered kinetically that nucleophilic attach under formation of hemiacetals, **13**, occurs exclusively. The hemiacetals react further to give aromatic compounds **14**.[26]

Example 3: According to the stated rules, the nitration of various methylbenzenes (Scheme IX), for example, **15**, with nitrylacetate results in formation of σ-complex **16** with the sterically more demanding and electropositive CH_3 ligand in the quasiaxial position. Because of the poor leaving tendency of the CH_3^+ group, rearomatization to give **17** does not occur, and instead nucleophilic attack results in formation of **18**.[27]

In conclusion this study has combined experimental and theoretical methods to provide a better understanding of the interactions of steric and electronic effects that govern the properties of σ-complexes (cyclohexadienylium ions), important intermediates in the electrophilic substitution reactions for aromatic compounds. Considerations of the concepts elucidated combined with molecular modeling techniques at the semiempirical level should prove to be of considerable predictive value for designing chemical reactions and predicting the properties of the products.

Acknowledgment. We thank P. Kollat and A. Meier for technical assistance in the course of the experimental work.

Registry No. 2a, 26812-57-7; **2b**, 87176-46-3; **2c**, 83927-54-2; **2d**, 87176-51-0; **2e**, 87176-50-9; **2f**, 105970-37-4; **2g**, 105970-38-5; **2h**, 77023-09-7; **2i**, 105970-39-6; **2j**, 105970-40-9; **2k**, 71-43-2; **2l**, 108-88-3; **2m**, 105970-41-0; **2n**, 55563-53-6; **2o**, 105970-42-1; **2p**, 105970-43-2; **2q**, 105970-44-3; **2r**, 105970-45-4; **2s**, 65963-62-4; **2t**, 105970-46-5; **2u**, 105970-47-6; **2v**, 105970-48-7; **3a**, 105991-10-4; **3b**, 105970-49-8; **4a**, 105970-51-2; **5**, 20758-47-8; **8a**, 105970-52-3; **8b**, 105970-53-4; **8c**, 105970-54-5; **8d**, 105970-55-6; **8e**, 105970-56-7; **8f**, 105970-57-8; **8g**, 105970-58-9; **8h**, 105970-59-0; **8i**, 105970-60-3; **8j**, 105970-61-4; **8k**, 105970-62-5; **9a**, 27175-04-8; **9b**, 27084-06-6.

Supplementary Material Available: Anisotropic temperature factors for non-hydrogen atoms and fractional atomic coordinates and isotropic temperature factors for H atoms for **3a**, **3b**, **4a**, and **5** (19 pages); observed and calculated structure factor tables for **3a**, **3b**, **4a**, and **5** (206 pages). Ordering information is given on any current masthead page.

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Communications to the Editor

Polarization in the Excited State of 1,3-Pentadiene: Experimental Evidence for an Allyl Cation–Methylene Anion Species

Michael E. Squillacote* and Thomas C. Semple

Department of Chemistry, Brown University
Providence, Rhode Island 02912

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Zwitterionic excited states have been postulated as intermediates in a variety of photochemical reactions, including those comprising the visual process.[1-7] The "sudden polarization" phenomenon described by Salem,[1] which intimately involves zwitterionic excited states, was based on the work of Dauben[4] involving the photochemistry of 1,3-dienes. There has, however, been very little other experimental evidence for the involvement of zwitterionic intermediates in the photochemistry of this seminal system.[8,9] We wish to report here regioselective photochemistry of an unsymmetrical 1,3-diene which enables us to infer the excited-state charge distribution of the predicted allylmethylene species.

The first suggestion that geometrical relaxation in the excited state of a 1,3-diene caused a highly polar twisted allylmethylene species was made by Dauben in 1970.[4] Because high stereospecificity was observed in the photocyclization of *trans*-3-ethylidenecyclooctene,[13] a zwitterionic excited state consisting of an allyl anion and a methylene cation was proposed. In light of this, Dauben also proposed an excited state of this type for the

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