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A MNDO STUDY OF THE STRUCTURES AND STABILITIES OF SOME SUBSTITUTED PENTADIENYL ANIONS *

MICHAEL J.S. DEWAR *, MARYE ANNE FOX * and DONNA J. NELSON **

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712 (U.S.A.)

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Summary

A MNDO study of the structures and stabilities of a series of pentadienyl anions has predicted that the W geometric form is more stable than the S or U forms by about 1.0 and 3.7 kcal/mol, respectively. Substitution of methyl for hydrogen in the 1- and 3-positions of pentadienyl anions has been found to stabilize the anion but less effectively than in the cations. Stabilization of the anion by alkyl (~1-2 kcal/mole) was less than that observed upon substitution of phenyl (~11 kcal/mole). Polarization, rather than negative hyperconjugation or induction, is probably the most important stabilizing factor. Charge density in the pentadienyl anion and cation follows the order: 3- > 1- > 2-position. Charge alternation increases significantly upon substitution so that the same order of charge densities is found, with significantly more negative charge borne at the 3- and 1-positions in substituted anions.

Introduction

This paper reports a detailed study of various substituted 2,4-pentadienyl anions by the MNDO semiempirical SCF MO method [1,2], carried out in the hope of elucidating the effects of alkyl groups on the stabilities and conformations of anions [3]. It therefore seems likely that it would provide useful information in the present case. For comparison, we have also carried out calculations for many of the corresponding cations.

The electronic nature of the methyl substituent continues to generate controversy. It has been clearly demonstrated that marked differences exist between solution and gas phase acidities of alcohols [4] and amines [5] and hence that the traditional postulation of solution-phase inductive electron release by methyl

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to anionic as well as cationic centers is probably wrong. The methyl group has in fact proved to be a most versatile substituent and has been considered best understood as polarizable [6]. Several theoretical and experimental studies have suggested the possible importance of hyperconjugation [7] and steric and conjugative effects (non-bonded interactions) on anion geometry [8] and in determining anion stability. It has also been pointed out that donation or withdrawal of electrons by alkyl groups bound to unsaturated carbon may be controlled by a delicate balance of EA (electron affinity) and ΔH° [9] and that the primary effect of alkyl groups (as acid-strengthening) may lie in their steric rather than electronic properties [10].

Several theoretical studies of the structure of the pentadienyl anion are available. The first of these, a study of conformational and isomer stability in pentadienyl anions by Hoffmann and Olofson [11], predicted that since the "non-bonding" pentadienyl π -orbital is 1,5 bonding, net stabilization of the pentadienyl anion should result if centers 1 and 5 approach close enough for significant $2p_z$ orbital overlap. If this geometry could be attained, the resulting "U"-shaped anion (1) should then be preferred over the "sickle"- (2) and "W"- (3) shaped planar conformations.

Although early evidence from base-catalyzed equilibration of several olefins suggested that the U-form was indeed stabilized [12] and although spectral evidence for U-shaped anions is available in some isoelectronic heteroatom-containing conjugated systems [13] or in systems with heteroatomic substituents on the carbon skeleton [14], NMR studies have conclusively shown that in solution the parent pentadienyl anion (associated with several different cations) exists predominantly in a W conformation [15]. Several alkyl- and phenyl-substituted pentadienyl anions have also been shown to prefer W or S conformations [16].

Several other groups have tried to solve this problem by theoretical calculations but so far these have not been carried out by procedures that could lead to quantitatively reliable results. Since the relevant differences in energy between isomeric ions are quite small, they can be usefully estimated only if a theoretical procedure of sufficient accuracy is used and if geometries are completely optimized without making any assumptions. So far, with one exception, calculations in this area have been carried using CNDO/2, a method which is known to give geometries and energies which in many cases are not merely inaccurate but ridiculous*. The one exception, a study by Bongini et al. [8d] of pentadienyllithium and the pentadienyl anion, made use of the Roothaan-Hall SCF method with the STO-3G basis set. This procedure usually gives reasonable estimates of the relative energies of isomeric species provided they contain no unusual types of bonds or strained rings. Their calculations are, however, vitiated by the drastic assumptions they made in calculating geometries. Thus while they concluded,

* For example linear CO_2 is predicted by CNDO/2 to be unstable, rearranging exothermically to a cyclic carbene, $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{array}$: [17a]). The errors in the relative energies calculated for isomeric "classical" and "nonclassical" carbocations also commonly amount to several eV. It is difficult to see why this procedure continues to be used for the calculation of energies and geometries of molecules, given the overwhelming superiority of more recent methods which require no more computing time, (e.g. $(\text{CH})_5^-$: [17b]).

apparently correctly, that the *W* form of the anion is more stable than the *S* (by 5 kcal/mol), their value for the *U* form was too positive, placing it 30 kcal/mol above the *W*. Their conclusion that a nonplanar spiral-*U* isomer of the covalent lithium derivative is lower in energy than the *W* (by 12 kcal/mol) is therefore of dubious reliability. They suggested on the basis of this calculation that such a species might be involved in certain base-catalyzed isomerizations [12], and sigmatropic rearrangements [13] which seem to take place via *U*-type intermediates.

While CNDO/2 cannot be regarded as a meaningful procedure for the calculation of molecular energies, it does seem to give reasonable descriptions of electron distributions in molecules. Grunwell and Sebastian [8i] have used it in this way to study the effects of substituents in the allyl, pentadienyl, and heptatrienyl anions and cations, using CNDO/2. They found methyl to be electron-withdrawing (relative to hydrogen) when attached to an anion and electron-releasing when attached to a cation. The effects are larger, as expected, when methyl is attached to an active position in the odd AH (alternant hydrocarbon) ion. In each case, approximately half the electron withdrawal or release was by the π route and half by σ . The transfer of charge affected all the carbon atoms in the ion in a similar manner, the carbon atom adjacent to methyl becoming more positive in the case of a cation and less negative in the case of an anion. This result is in agreement with the results of NMR studies of pentadienyl anion and its methyl derivatives [15e] which suggest that attachment of methyl to a given carbon atom makes the latter less negative. However it now appears that this may have been due to ion pairing since addition of dimethyl ether (which complexes Li^+) reduces or reverses the effect [18].

Several other theoretical studies of pentadienyl anions have also been reported but these have been of a more qualitative nature or based on the σ, π approximation. We therefore decided to reinvestigate the problem in more detail, using procedures (MINDO/3 [19] and MNDO [2]) which have been developed in these laboratories and without making any geometrical assumptions.

Procedure

The calculations were carried out using the standard MNDO [2] and MINDO/3 [19] procedures, geometries being found by minimizing the energy, with respect to all geometrical coordinates, using our standard Davidon—Fletcher—Powell (DFP) optimization procedure and without making any assumptions of any kind.

Results

Table 1 shows the heats of formation calculated for the pentadienyl cation and anion and for a number of their methyl derivatives, using MNDO and MINDO/3.

Previous experience [19,20] has indicated that MINDO/3 gives remarkably good results for carbocations of all kinds, both "classical" and "non-classical", while MNDO does quite well for the "classical" ions but gives heats of formation for the "non-classical" ones that tend to be too positive [20c]. Indeed, the MNDO results for the latter are similar to those given by the Roothaan—Hall

TABLE 1
HEATS OF FORMATION CALCULATED USING MNDO (MINDO/3) ^a




		ΔH_f		ΔH_f		ΔH_f		ΔH_f
	1	23.25		15	-9.71		29	29.77
	2	15.34		16	-6.47		30	35.48
	3	-9.70		17	6.20		31	2.15
	4	-6.95		18	6.78		32	9.44
	5	-4.13		19	14.42		33	10.74
	6	20.51		20	8.12		34	8.61
	7	13.32		21	18.86 (19.20)		35	29.52
	8	-11.82		22	6.54 (6.54)		36	18.10
	9	-8.89		23	11.86 (17.41)		37	(219.29)
	10	-8.62		24	12.19		38	(216.55)
	11	-5.58		25	13.14 (18.93)		39	(215.14)
	12	19.55		26	9.65		40	(198.17)
	13	12.68		27	23.96		41	(196.42)
	14	-12.54		28	24.77		42	(212.58)
							43	(210.38)

^a Figures in parentheses are MINDO/3 calculations.

(RH) method using the 4-31G basis set [20c]. Therefore when there is a discrepancy between the MINDO/3 and MNDO results for carbocations, the MINDO/3 are likely to be the better.

In the case of anions, on the other hand, MNDO seems to do well, except for

TABLE 2
STABILIZING EFFECT OF ALKYL SUBSTITUENTS IN W CONFORMERS OF PENTADIENYL IONS

	Ion alkyl group	Relative stabilization energy (kcal/mol) for alkyl in position		
		1	2	3
	CH ₃	6.1	0.8	4.5
	CH ₃	1.0	-1.9	1.2
	C ₂ H ₅	—	—	2.2

a few very small ones where the charge is essentially localized on a single atom (e.g. HO⁻, HS⁻, Cl⁻) [3]. In the latter, the calculated energies are too positive by ca. 1 eV, due, we believe, to the failure of MNDO to allow for the increase in size of the AOs of an atom carrying a full unit of negative charge. Any dispersal of the charge is sufficient to neutralize the error. Thus the heats of formation even of ions as small as CH₃O⁻ are well reproduced. Errors in the relative energies of isomer relative anions given by MNDO are therefore likely to be as small as those for neutral molecules [2].

Table 1 also shows heats of formation calculated for the conjugated dienes from which the pentadienyl anions and cations can be derived by loss of H⁺ or H⁻, respectively. The relative heats of reaction (ΔH) for the latter processes should depend only on the relative resonance energies of the ions and so provide information concerning the stabilizing or destabilizing effect of substituents in them. Values of ΔH for the methylpentadienyl ions are listed in Table 2, relative to those for the parent pentadienyl ions. It will be seen that a methyl group in an active (1,3,5) position of either ion has a stabilizing effect, this being greatest in the 3-position. In the 2-position, methyl marginally stabilizes the cation but destabilizes the anion.

The calculated carbon-carbon bond lengths in these ions are listed in Table 3. Bond lengths for the remaining ions and Cartesian coordinates for all the species studied are available as supplementary information.

Table 4 shows the calculated distribution of formal charges in some of the ions studied, at their calculated equilibrium geometries. Values for the remaining ions are also available as supplementary material. Note that the formal charge is greatest at the active positions in each ion, the other carbon atoms having charges which are not only numerically less but often of opposite sign. Such alternation of charge is commonly observed in SCF calculations for ions, especially for conjugated ions of odd alternant type [8i].

The only metal for which MNDO parameters are currently available is beryllium [21]. Calculations were carried out for species derived from the various pentadienyl anions by combination with HBe⁺, this serving as a model for the lithium cation. The calculated heats of formation and geometries of the adducts and the corresponding distributions of formal charge are also displayed in Tables 1, 3 and 4.

(Continued on p. 170)

TABLE 3
 BOND DISTANCES CALCULATED USING MNDO/3^k

Com- pound	C(1)-C(2)	C(2)-C(3)	C(3)-C(4)	C(4)-C(5)	C(1)- H _{cis} trans	C(2)-H	C(3)-H	C(4)-H	C(5)- H _{cis} trans	Bond distances in substituents
1	1.377	1.409	1.409	1.377	1.083 1.089	1.377	1.409	1.409	1.083 1.089	
2	1.370	1.425	1.427	1.370	1.084 1.900	1.106	1.496	1.106	1.090 1.084	1.117 ^a 1.117 1.114
3	1.378	1.426	1.426	1.377	1.090 1.485	1.105	1.500	1.106	1.090 1.485	1.117 ^a 1.117 1.114 1.113 ^c 1.116 1.114
4	1.377	1.423	1.430	1.373	1.483 1.098	1.108	1.497	1.105	1.090 1.485	1.117 ^a 1.117 1.114 1.113 1.116 1.109 ^b 1.116 ^c
5	1.373	1.428	1.427	1.374	1.483 1.097	1.107	1.496	1.108	1.483 1.097	1.118 ^a 1.118 1.111 1.114 1.113 1.113 ^c 1.111 1.117
6	1.379	1.411	1.410	1.410	1.086 1.088	1.100	1.096	1.103	1.085 1.085	
7	1.372	1.426	1.428	1.372	1.085 1.089	1.102	1.495	1.105	1.084 1.089	1.118 ^a 1.118 1.110
8	1.380	1.424	1.428	1.379	1.091 1.485	1.102	1.497	1.105	1.090 1.485	1.117 ^a 1.116 1.116 1.113 1.113 ^c
9	1.379	1.422	1.429	1.378	1.480 0.098	1.103	1.499	1.109	1.481 1.098	1.117 ^a 1.114 ^b 1.114 1.113 1.116 1.116 ^c
10	1.379	1.422	1.431	1.379	1.480 1.098	1.105	1.497	1.105	1.090 1.485	1.117 ^a 1.114 ^b 1.117 1.114 1.116 1.115 ^c
11	1.381	1.423	1.427	1.378	1.090 1.485	1.099	1.500	1.108	1.480 1.098	1.117 ^a 1.115 ^b 1.117 1.116 1.113 1.113 ^c
12	1.380	1.411	1.411	1.380	1.086 1.088	1.101	1.094	1.101	1.086 1.088	1.110 1.114 1.116 1.114

13	1.373	1.426	1.429	1.373	1.084	1.104	1.492	1.103	1.085	1.117 ^a
					1.089				1.089	1.117
										1.112
14	1.380	1.426	1.429	1.380	1.091	1.104	1.494	1.103	1.091	1.116 ^a
					1.485				1.484	1.116
										1.115
										1.113
15	1.380	1.428	1.427	1.379	1.090	1.104	1.492	1.107	1.481	1.116 ^a
					1.485				1.098	1.116
										1.113
										1.116
16	1.378	1.427	1.430	1.378	1.480	1.108	1.491	1.107	1.481	1.115 ^a
					1.098				1.098	1.115
										1.114
										1.113
17	1.378	1.414	1.408	1.388	1.086	1.101	1.095	1.101	1.091	1.116 ^c
					1.088				1.481	1.116
										1.114
18	1.377	1.415	1.407	1.386	1.086	1.101	1.094	1.103	1.480	1.116 ^c
					1.088				1.094	1.116
										1.115
19	1.399	1.419	1.410	1.383	1.086	1.506	1.098	1.099	1.085	1.115 ^d
					1.087				1.088	1.115
										1.108
20	1.373	1.428	1.428	1.373	1.085	1.104	1.503	1.104	1.085	1.118 ^f
					1.089				1.089	1.119
										1.537 ^e
21	1.407	1.351	1.466	1.345	1.111	1.095	1.095	1.096	1.089	
					1.111	1.113	1.113	1.113	1.089	
					1.109				1.100	
(21)	1.473	1.344	1.463	1.330	1.112	1.093	1.095	1.095	1.099	1.111 ^c
					1.113				1.093	1.111
					1.111				1.494	1.110
22	1.493	1.382	1.444	1.382	1.111	1.113	1.114	1.113	1.113	1.112 ^c
					1.111				1.472	1.113
					1.111					1.111
(22)	1.472	1.345	1.462	1.344	1.113	1.503	1.098	1.094	1.087	1.113 ^d
					1.112				1.088	1.114
					1.111					1.107
23	1.509	1.393	1.442	1.374	1.111	1.495	1.116	1.113	1.110	1.112 ^d
					1.111				1.099	1.113
					1.109					1.111

TABLE 3 (Continued)

Com- pound	C(1)-C(2)	C(2)-C(3)	C(3)-C(4)	C(4)-C(6)	C(1)- H ^{cis}	C(2)-H	C(3)-H	C(4)-H	C(5)- H ^{cis} H ^{trans}	Bond distances in substituents
(23)	1.499	1.362	1.463	1.330	1.112 1.113 1.111	1.508	1.099	1.094	1.113 1.112 1.108	1.110 ^d 1.111 1.112
24	1.386	1.454	1.379	1.494	1.087 1.089	1.097	1.508	1.096	1.089 1.089	1.111 ^a 1.110
25	1.497	1.355	1.484	1.340	1.110 1.110 1.110					1.109
(25)	1.473	1.363	1.491	1.330	1.113 1.113 1.110	1.114	1.497	1.114	1.100	1.112 ^a 1.112 1.111
26	1.494	1.392	1.461	1.369	1.110 1.110 1.110	1.095	1.517	1.098	1.086 1.089	1.115 ^f 1.115 1.534 ^e
27	1.353	1.454	1.401	1.403	1.086 1.090	1.102	1.496	1.102	1.094 1.429	1.115 ^a 1.115 1.109
28	1.354	1.451	1.404	1.398	1.085 1.090	1.103	1.495	1.103	1.093 1.435	1.115 ^c 1.115 1.109
29	1.357	1.451	1.403	1.397	1.085 1.090	1.103	1.494	1.109	1.434 1.099	1.116 ^a 1.115 1.110
30	1.496	1.356	1.465	1.347	1.111 1.111	1.097	1.508	1.096	1.096 1.479	1.111 ^a 1.110 1.109 1.091 1.091

81	1.504	1.356	1.472	1.375	1.118	1.094	1.091	1.099	1.115	1.302/	1.109	1.404	1.090
					1.119				1.098			1.418	1.092
					1.722							1.405	1.091
												1.406	
82	1.495	1.383	1.443	1.371	1.222	1.095	1.097	1.098	1.086	1.276/			
					1.119				1.088				
					1.674								
83	1.373	1.447	1.382	1.496	1.087	1.111	1.095	1.095	1.122	1.282/			
					1.087				1.122				
									1.680				
84	1.493	1.385	1.444	1.372	1.122	1.096	1.095	1.096	1.087	1.276/			
					1.120				1.088				
					1.674								
85	1.487	1.481	1.413	1.392	1.090	1.118	1.094	1.096	1.086	1.276/			
					1.090	1.704			1.086				
86	1.364	1.527	1.491	1.344	1.090	1.093	1.118	1.097	1.088	1.282/			
					1.108		1.710		1.089				
(87)	1.352	1.421	1.421	1.353	1.101	1.109	1.115	1.109	1.101				
					1.099				1.099				
(88)	1.354	1.421	1.419	1.354	1.100	1.108	1.114	1.109	1.100				
					1.100				1.100				
(89)	1.354	1.418	1.419	1.354	1.100	1.107	1.115	1.107	1.100				
					1.099				1.099				
(40)	1.349	1.427	1.405	1.381	1.100	1.108	1.115	1.109	1.462	1.110 ^c			
					1.099				1.113	1.110			
										1.107			
(41)	1.349	1.428	1.405	1.381	1.100	1.108	1.114	1.108	1.114	1.110 ^c			
					1.099				1.461	1.110			
										1.107			
(42)	1.372	1.438	1.423	1.353	1.101	1.504	1.117	1.108	1.101	1.108 ^d			
					1.101				1.100	1.109			
					1.101					1.108			
(43)	1.350	1.450	1.453	1.349	1.100	1.111	1.482	1.110	1.100	1.110 ^a			
					1.099				1.099	1.110			
										1.107			

^a C—H bond distances in 3-Me, ^b C—H bond distances in 1-Me, ^c C—H bond distances in 5-Me, ^d C—H bond distances in 2-Me, ^e C—C bond distance in 3-Et, ^f C—H₂ bond distances in 3-Et, ^g C—H₃ bond distances in 3-Et, ^h C—C bond distances in 5-Ph, ⁱ C—H bond distances in 5-Ph, ^j C—H bond distances in 5-Ph, ^k Be—h bond distance, ^l Compound numbers in parentheses indicate MINDO/3 calculations.

TABLE 4

DISTRIBUTION OF FORMAL CHARGE CALCULATED USING MNDO(MINDO/3)^k

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C or H ^{cis} _{trans} at C(1)	C or H
1	-0.282	-0.011	-0.315	-0.011	-0.282	0.014 -0.022	-0.032
2	-0.281	0.049	-0.432	0.048	-0.281	0.018 -0.019	-0.031
3	-0.342	0.089	-0.423	0.089	-0.344	0.036 0.038	-0.026
4	-0.353	0.103	-0.453	0.106	-0.319	0.034 0.140	-0.027
5	-0.327	0.117	-0.479	0.117	-0.331	0.142 -0.002	-0.033
6	-0.300	-0.010	-0.314	-0.021	-0.292	-0.001 -0.015	-0.006
7	-0.305	0.051	-0.416	0.037	-0.292	0.004 -0.014	-0.009
8	-0.367	0.094	-0.408	0.079	-0.355	0.022 0.141	-0.004
9	-0.365	0.092	-0.405	0.083	-0.348	0.022 0.141	-0.004
10	-0.364	0.102	-0.410	0.081	-0.354	0.152 -0.001	-0.010
11	-0.362	0.102	-0.409	0.087	-0.348	0.152 -0.001	-0.010
12	-0.295	-0.025	-0.308	-0.025	-0.295	0.002 -0.016	-0.015
13	-0.301	0.039	-0.410	0.036	-0.297	0.007 -0.015	-0.019
14	-0.362	0.081	-0.402	0.077	-0.358	0.110 0.024	-0.015
15	-0.355	0.085	-0.404	0.083	-0.362	0.149 -0.002	-0.020
16	-0.359	0.092	-0.407	0.088	-0.354	0.151 -0.003	-0.022
17	-0.277	-0.018	-0.304	0.014	-0.374	0.005 -0.013	-0.011
18	-0.277	-0.016	-0.308	0.017	-0.371	0.005 -0.013	-0.011

C or H	C or H	C or H ^{cis} at C(5) <i>trans</i>	Charge on substituents		
-0.023	-0.032	0.014 -0.022			
0.176	-0.030	0.018 -0.019	-0.076 ^a -0.077 -0.063		
0.166	-0.026	0.036 0.137	-0.069 ^a -0.070 -0.058	-0.052 ^b -0.049 -0.055	-0.062 ^c -0.049 -0.055
0.175	-0.032	0.142 -0.004	-0.073 ^a -0.073 -0.059	-0.054 ^b -0.056 -0.059	-0.020 ^c -0.048 -0.069
0.181	-0.033	0.144 -0.002	-0.074 ^a -0.076 -0.061	-0.045 ^b -0.026 -0.059	-0.029 ^c -0.045 -0.068
-0.006	-0.026	0.007 0.018			
0.175	-0.024	0.010	-0.076 ^a -0.076 -0.050		
0.168	-0.020	0.028 0.139	-0.055 ^a -0.055 -0.057	-0.070 ^b -0.070 -0.045	-0.056 ^c -0.056 -0.054
0.166	-0.026	0.148 -0.004	-0.054 ^a -0.054 -0.057	-0.070 ^b -0.070 -0.045	-0.043 ^c -0.043 -0.064
0.168	-0.020	0.028 0.139	-0.049 ^a -0.049 -0.064	-0.070 ^b -0.070 -0.045	-0.055 ^c -0.055 -0.054
0.167	-0.026	0.148 -0.003	-0.048 ^a -0.049 -0.064	-0.070 ^b -0.070 -0.045	-0.043 ^c -0.042 -0.065
0.007	-0.015	0.002 -0.016			
0.179	-0.018	0.007 -0.015	-0.069 ^a -0.069 -0.055		
0.173	-0.014	0.024 0.140	-0.055 ^a -0.055 -0.055	-0.063 ^b -0.063 -0.050	-0.055 ^c -0.055 -0.055
0.172	-0.015	0.025 0.140	-0.055 ^a -0.055 -0.055	-0.063 ^b -0.062 -0.050	-0.045 ^c -0.046 -0.064
0.172	-0.020	0.149 -0.002	-0.045 ^a -0.045 -0.064	-0.062 ^b -0.062 -0.050	-0.047 ^c -0.047 -0.064
0.011	-0.015	0.017 0.150	-0.062 ^c -0.062 -0.061		
0.012	-0.018	0.156 -0.002	-0.053 ^c -0.053 -0.069		

TABLE 4 (Continued)

Com- pound	C(1)	C(2)	C(3)	C(4)	C(5)	C or H ^{cis} at C(1) <i>trans</i>	C or H
19	-0.243	-0.137	-0.236	-0.055	-0.273	0.000 -0.016	0.128
20	-0.298	0.035	-0.399	0.036	-0.299	0.007 -0.014	0.017
21	0.064	-0.102	-0.051	-0.079	-0.050	-0.002 -0.002 -0.005	0.050
(21)	0.098	0.000	0.019	0.038	-0.035	-0.027 -0.027 -0.026	-0.022
22	0.064	-0.105	-0.052	-0.052	-0.105	-0.001 -0.001 -0.005	0.051
(22)	0.099	-0.001	0.022	0.022	-0.001	-0.027 -0.027 -0.027	-0.017
23	0.073	-0.144	-0.034	-0.072	-0.058	-0.003 -0.003 -0.006	0.079
(23)	0.087	0.003	0.013	0.036	-0.030	-0.026 -0.026 -0.030	0.085
24	-0.046	-0.107	-0.038	-0.106	-0.064	0.041 0.040	0.078
25	-0.056	-0.072	-0.096	-0.083	0.064	0.043 0.039	0.053
(25)	0.096	-0.005	0.020	0.027	-0.037	-0.026 -0.026 -0.025	-0.020
26	-0.058	-0.064	-0.072	-0.091	0.064	0.000 0.000 -0.006	0.046
27	-0.352	0.156	-0.389	0.066	-0.239	0.026 0.117	-0.005
28	-0.361	0.158	-0.402	0.072	-0.249	0.029 0.112	-0.007
29	-0.367	0.162	-0.398	0.071	-0.248	0.121 0.009	-0.024

C or H	C or H	C or H ^{cis} at C(5) ^{trans}	Charge on substituents		
0.001	-0.009	0.002 -0.015	-0.056 ^d -0.056 -0.036		
0.120	-0.018	0.007 -0.014	-0.041 ^f -0.043 -0.038 ^z	-0.021 ^g -0.021 -0.059	
0.048	0.049	0.041 0.039			
-0.017	-0.020	0.007 0.011			
0.049	0.049	0.051 0.064	-0.001 ^c -0.001 -0.005		
-0.023	-0.023	-0.017 0.099	-0.027 ^c -0.027 -0.027		
0.042	0.051	0.042 0.040	-0.002 ^d -0.003 -0.005		
-0.028	-0.021	0.007 0.010	-0.026 ^d -0.026 -0.029		
0.042	0.053	-0.001 -0.002 -0.005	-0.004 ^d -0.004 -0.004		
0.079	0.047	-0.001 -0.001 -0.005	-0.003 ^a -0.003 -0.004		
0.082	-0.023	0.005 0.011	-0.025 ^a -0.025 -0.030		
0.027	0.044	0.043 0.039	0.004 ^f 0.006 0.032 ^e	-0.003 ^g -0.003 -0.007	
0.158	0.001	0.0004 0.021	-0.057 ^a -0.054 -0.032	-0.124 ^h -0.042 -0.141 -0.045 -0.168	0.052 ⁱ 0.026 0.035 0.022 0.027
0.162	-0.002	-0.001 0.019	-0.057 ^a -0.058 -0.037	-0.142 ^h -0.036 -0.139 -0.040 -0.173	0.041 ⁱ 0.024 0.038 0.023 0.028
0.159	-0.004	-0.002 0.021	-0.056 ^a -0.055 -0.034	-0.157 ^h -0.028 -0.152 -0.033 -0.187	0.037 ⁱ 0.022 0.035 0.021 0.027

TABLE 4 (Continued)

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C or H ^{Cis} _{trans} at C(1)	C or H at C(1)
30	-0.044	-0.045	-0.099	-0.081	0.063	0.055 -0.053	0.055
31	-0.245	0.040	-0.189	0.104	-0.130	0.278 0.024 0.020	0.049
32	-0.234	-0.062	-0.071	-0.068	-0.064	0.485 -0.023 -0.023	0.041
33	-0.053	-0.059	-0.088	-0.039	-0.240	0.048 0.044	0.050
34	-0.234	-0.064	-0.074	-0.068	-0.064	0.024 0.024 0.486	0.041
35	-0.128	-0.249	-0.055	-0.076	-0.074	0.048 0.046	0.060 0.489
36	-0.140	-0.014	-0.257	-0.044	-0.094	0.058 0.081	0.071
(37)	0.244	-0.126	0.394	-0.126	0.245	0.026 0.068	0.081
(38)	0.262	-0.129	0.393	-0.123	0.254	0.042 0.063	0.060
(39)	0.257	-0.125	0.397	-0.125	0.257	0.039 0.064	0.072
(40)	0.315	-0.160	0.376	-0.114	0.221	-0.019 -0.024	0.065
(41)	0.324	-0.163	0.376	-0.115	0.219	-0.005 -0.019	0.062
(42)	0.218	-0.077	0.370	-0.120	0.249	0.035 0.058	0.066
(43)	0.229	-0.132	0.393	-0.133	0.222	0.031 0.062	0.056

^a Charges on protons in 3-Me. ^b Charges on protons in 1-Me. ^c Charges on proton in 5-Me. ^d Charges on protons in 2-Me. ^e Charge on terminal C in 3-Et. ^f Charges on protons of CH₂ in 3-Et. ^g Charges on protons of CH₃ in Et. ^h Charges on C's in 5-Ph. ⁱ Charges on protons in 5-Ph. ^j Charge on proton in Be-H. ^k Compound numbers in parentheses indicate MINDO/3 calculations.

Discussion

A. Geometry of pentadienyl anions

MNDO agrees with experiment and other calculations (see above) in predict-

C or H at C(2)	C or H at C(3)	C or H ^{cis} at C(4) <i>trans.</i>	Charge on substituents		
0.079	0.047	-0.001 -0.001	-0.003 ^a -0.003 -0.003	-0.040 ^h -0.065 -0.039 -0.065 -0.053	0.059 ⁱ 0.060 0.059 0.060 0.061
0.072	0.064	0.105 0.070	-0.263 ^j		
0.044	0.044	0.038 0.041	-0.240 ^j		
0.053	0.043	0.023 0.023 0.442	-0.248 ^j		
0.046	0.047	0.038 0.041	-0.240 ^j		
0.044	0.047	0.040 0.039	-0.231 ^j		
0.050 0.414	0.035	0.039 0.035	-0.234 ^j		
0.019	0.080	0.026 0.058			
0.004	0.075	0.033 0.065			
-0.013	0.072	0.039 0.064			
-0.023	0.064	0.035 0.061	0.055 ^c 0.054 0.056		
-0.014	0.062	0.036 0.060	0.063 ^c 0.063 0.051		
-0.021	0.067	0.038 0.062	0.024 ^d 0.025 0.004		
-0.053	0.058	0.029 0.063	0.068 ^a 0.067 0.041		

ing the order of stability of the pentadienyl anions to be $W > S > U$. The differences in energy between them calculated by MNDO ($W \rightarrow S$, 1.0 kcal/mol; $W \rightarrow U$, 3.7 kcal/mol) are, however, considerably less than those estimated by other workers (e.g. 5 and 30 kcal/mole by Bongini et al. [8d]) or expected on the basis

of simple electrostatic repulsion between the terminal carbon atoms ($W \rightarrow U$, ~ 6.9 kcal/mol *). As noted above, the experimental evidence seems to suggest that the isomers indeed differ in energy by only small amounts.

MINDO/3 predicts a similar relationship between the corresponding cations, the S and U isomers being less stable than the W by 1.4 and 4.2 kcal/mol, respectively. The fact that the $W \rightarrow U$ differences are similar for the anions and cations implies that exchange interactions between the terminal carbon atoms must be negligible in the U isomers since such interactions would stabilize the anion and destabilize the cation [22].

B. Resonance energies of odd conjugated species

The resonance energy of a molecule is commonly defined as the difference ($\Delta H_f^0 - \Delta H_f$) between its heat of formation (ΔH_f) and that (ΔH_f^0) of a "non-resonating" analog. There is, however, no unambiguous way in which the properties of such an imaginary species can be determined. In the case of even conjugated hydrocarbons, this difficulty can be overcome by adopting as a model the corresponding "classical" polyene as the reference compound [23]. Since the bonds in classical polyenes are localized [23], their heats of formation can be estimated by summing appropriate "polyene" C—C, C=C, and C—H bond energies [23]. The same procedure can be used to calculate heats of formation of reference polyenes, e.g. of 1,3,5-cyclohexatriene in the case of benzene. Unfortunately no such reference system exists in the case of odd conjugated systems, in particular odd conjugated hydrocarbons, since the bonds in them are not localized. Many authors (e.g. Benson [24]) have estimated resonance energies of such species (e.g. allyl radical) by taking apparently analogous alkyl ions or radicals as the reference compounds. Thus primary radicals of the type $RCH_2\cdot$ are compared with ethyl($CH_3CH_2\cdot$). This procedure is, however, undesirable because such alkyl species are themselves stabilized by strong first order hyperconjugative interactions. The resulting "resonance energy" is then a mixture of two different quantities, i.e. the conjugative stabilization of the conjugated radical and the hyperconjugative stabilization of the reference species. The only solution seems to be the use of methyl as the reference species, this, the limiting case of an odd alternant hydrocarbon, having its unpaired electron localized on a single carbon atom. Furthermore, the heats of formation of all three forms of methyl (CH_3^+ , $CH_3\cdot$, CH_3^-) are all known, i.e. CH_3^+ , 262 [25], $CH_3\cdot$, 34.0 [26]; CH_3^- , 32.2 [27] kcal/mol.

The resonance energy ($RE_{RCH_2^{+-}}$) of a conjugated ion or radical, RCH_2^{+-} , can then be defined as the difference between its heat of formation from RCH_3 , and that of the corresponding methyl species (CH_3^{+-}) from methane (ΔH_f , -17.9 kcal/mol [28]) Thus:

$$\begin{aligned} RE_{RCH_2^+} &= \Delta H_f(CH_3^+) - \Delta H_f(CH_3) - [\Delta H_f(RCH_2^+) - \Delta H_f(RCH_3)] \\ &= 280 - \Delta H_f(RCH_2\cdot) + \Delta H_f(RCH_3) \end{aligned}$$

* Calculated for a simple model with bond lengths 1.4 Å, bond angles 120° , and charges of $-e/3$ on C(1), C(3), and C(5).

Likewise:




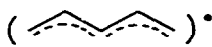


$$RE_{RCH_2^\cdot} = 52 - \Delta H_f(RCH_2^\cdot) + \Delta H_f(RCH_3)$$

$$RE_{RCH_2^-} = 50 - \Delta H_f(RCH_2^-) + \Delta H_f(RCH_3)$$

Table 5 compares calculated and observed heats of formation, and resonance energies estimated in this way, for three odd alternant hydrocarbon species, namely allyl ($R = CH_2=CH$), pentadienyl ($R = CH_2=CHCH=CH$) and benzyl ($R = Ph$). Because of our use of methyl as reference, the resonance energies are larger than those usually quoted, by the hyperconjugative stabilization of the corresponding ethyl species. Thus the experimental "ethyl" values for allyl and pentadienyl radicals are 10.2 and 12.3 kcal/mol, respectively.

Note that the resonance energy defined in this way depends on the point of protonation. This is taken into account by the formal definition. Thus the energy

TABLE 5
STABILIZATION ENERGIES OF ODD RADICALS AND IONS

Compound	MNDO	Stabilization energy (kcal/mol)	
		MINDO/3	Experiment [ref.]
 \cdot	21.5 ^a	14.5 ^a	16.2 [31,27]
 $^+$	29.0	16.3	27.1 [31,32]
 $-$	64	64	59 [31,33]
 \cdot	23.3 ^a	16.8 ^a	18.3 [31,34] ^b
 $-$	49.0	35.6	37.5 [31,35]
 $^+$	79	84	68 [31,34] ^b
PhCH ₂ \cdot	15.8 ^a	11.0 ^a	19 [31,36]
PhCH ₂ $-$	45.3	31.2	37 [31,37]
PhCH ₂ $^+$	76	83	76 [31,38]

^a Calculated using the half-electron method. ^b This value is calculated using the ionization potential of pentadienyl radical (7.76 eV) which is measured by electron impact. It can be noted that measurements taken in this way (i.e. 7176 for benzyl radical) appear to be too high by as much as 0.5 eV when compared with other experimental data. (See refs. 29, 30 and 33).

change on protonating pentadienyl anion at the central carbon atom, to form 1,4-pentadiene, is different from that on terminal protonation, forming 1,3-pentadiene. The former case, however, refers to the resonance energy of divinylmethyl anion, $(\text{CH}_2=\text{CH})_2\text{CH}_2^-$, in our system. This distinction provides a direct measure of the ease of protonation of such ambident anions at different positions. Table 5 shows both values for the pentadienyl species, corresponding to terminal and central attack.

C. Metal derivatives

As noted above, the relative stabilities of different isomeric ions in solution may differ from those in the gas phase, due to solvation and interaction with the gegenion. The effect of solvent cannot be assessed at present but that of the gegenion should be indicated by the results for BeH^+ derivatives of the ions shown in Table 1. It will be seen that in the BeH^+ adducts, the order of stability is different from that for the free ions, the U isomer now being much the most stable. This of course is not surprising, because while the U isomer is the most hindered form of the free ion, it is also the best suited geometrically to chelate to BeH^+ .

The geometries of the BeH^+ adducts are interesting. In all cases, the beryllium ion is covalently bound to C(1), C(3) or C(5) in the pentadienyl moiety, giving rise to a pentadienylberyllium hydride. However, the beryllium also interacts in π complex fashion with one of the double bonds in the U pentadienyl moiety. These points are illustrated in Fig. 1 by ORTEP plots of the U anion and its BeH^+

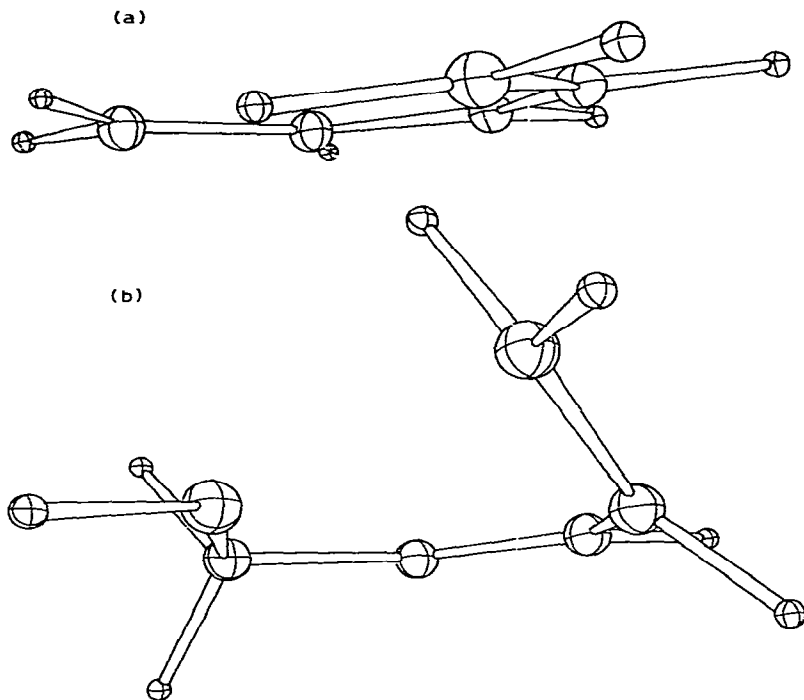


Fig. 1. ORTEP plots of (a) U-shaped pentadienyl anion; (b) BeH^+ adduct of U-shaped pentadienyl anion.

adduct. The π interaction would be expected to be strongest in the U isomer, for geometrical reasons, so it is not surprising that this should be the most stable of the isomeric beryllium derivatives.

D. Effect of alkyl substituents

The effect of alkyl substituents on the stabilities of the pentadienyl ions can be estimated from the differences in heat of formation between the ions and the corresponding derivatives of pentadiene; *vide supra*. Thus the effect of a methyl substituent can be deduced from the difference in heat of formation between the methylpentadienyl ion and the hexadiene formed from it by addition of H^+ or H^- . Table 2 shows values calculated in this way from the data in Table 1, by comparison with the corresponding difference in heat of formation between the parent pentadienyl ion and penta-1,3-diene. It will be seen that methyl substituents in the active (1,3,5) positions of either ion, in the unhindered W conformation, have a stabilizing effect, this being greatest in the 3-position where the negative charge in the parent ion is greater (Table 3). In the 2-position, methyl has a marginal stabilizing effect on the cation whereas in the anion it is quite strongly destabilizing.

Recent work has shown that alkyl substituents stabilize many anions in the gas phase. Thus alkoxide ions (RO^-) are weaker bases than hydroxide (HO^-), a direct reversal of the order observed in solution. The stabilization moreover increases with size of the alkyl group, basicity in the gas phase decreasing in the order $HO^- > CH_3O^- > C_2H_5O^- > (CH_3)_2CHO^- > (CH_3)_3CO^-$ [4]. It has been suggested that these effects reflect the polarizability of the alkyl group, the ion being stabilized by the resulting charge-dipole interaction and the polarizability of the alkyl group increasing with its size [4,6b]. Alkyl groups also stabilize cations, more so indeed than they do anions, a difference which has been commonly attributed to hyperconjugation and inductive effects. The $-I$ inductive effect of alkyl would be expected to lead to stabilization of cations but destabilization of anions, while hyperconjugation has usually been assumed to take place only in a sense corresponding to electron release by alkyl, due to an interaction between the filled CH bond MOs and empty antibonding orbitals of the substrate. It is, however, possible in principle for alkyl groups to stabilize anions likewise, this time through interactions between the empty antibonding CHMOs and the HOMOs of the anions [7d]. This possibility has been largely disregarded because it was until recently believed that the effect of alkyl groups on anions is inherently destabilizing. We now know that the inherent stabilizing effect of alkyl groups on anions is reversed by overriding solvent effects, accounting for the apparent destabilization of anions by alkyl groups in solution.

There seems little point in trying to assess these effects in a quantitative manner. Some idea of their relative importance can, however, be gained from the distributions of formal charge in the methylpentadienyl ions; see Table 6.

Hyperconjugation should lead to a net transfer of formal charge from the ion to methyl but only when methyl occupies an active position (1,3,5) in the alternating pentadienyl system. The distribution of this charge between C and H_3 of methyl will depend on the relative magnitudes of the interactions between the NBMO of pentadienyl and the bonding, and antibonding, CH MOs of the methyl group. If only the bonding, or only the antibonding, CH MOs interact, the

TABLE 6
DISTRIBUTION OF FORMAL CHARGE IN METHYLPENTADIENYL IONS

Ion	Net formal charges in anions			Net formal charges in cations		
	C ₅ H ₇	C	H ₃	C ₅ H ₇	C	H ₃
1-CH ₃	-0.965	+ 0.150	- 0.185	+0.842	- 0.019	+ 0.177
2-CH ₃	-0.980	+ 0.128	- 0.148	+0.879	+ 0.006	+ 0.054
3-CH ₃	-0.986	+ 0.179	- 0.193	+0.878	- 0.053	+ 0.176

charge will be shared more or less evenly; if both interact, the charge will be concentrated to a greater or less extent on the methyl hydrogens. Finally, polarity of the C-CH₃ bond, due to the different hybridization of the two carbon atoms, should lead to polarization in the sense C^{δ-}-CH₃^{δ+}.

On this basis the results for the anions in Table 6 indicate polarization to be predominant. Hyperconjugation and C-CH₃ bond polarity play only very minor roles, judging by the near-equality and opposite sign of the charges on C and H₃ in methyl and by the similar effects produced by methyl at all three positions. This at first sight might seem surprising since the charges at C(2) in the pentadienyl ions are small (Table 4). However, the polarization depends on the net electric field in the CH region of methyl. Calculation of this, using the charges listed in Table 4 and the calculated geometries from Table 5, shows it to be not much less for the 2-methylpentadienyl ions than for the 1- and 3-methyl ones.

Hyperconjugation thus seems to be unimportant in the anions indicating that the HOMO of pentadienyl, i.e. its π-NBMO, does not interact with the empty CH bond MOs of methyl. This is not in fact surprising because the latter are very much higher in energy than the NBMO. Since the same should be true also for the methylpentadienyl cations, any hyperconjugation in the latter should lead to depletion of the filled CH bonding MOs of methyl and so give rise to comparable positive charges on both C and H₃. The charge distributions for these ions (Table 6) indicate that hyperconjugation must then be comparable in importance with methyl polarization. This again is not surprising because the filled bonding CH MOs of methyl must be much closer in energy to the pentadienyl NBMO than are the empty antibonding ones.

A similar situation seems likely to occur generally, hyperconjugative stabilization of ions by alkyl being limited to cations. This conclusion has of course been generally held by organic chemists for some time but only because of the erroneous belief that alkyl substituents destabilize anions.

The results in Table 6 indicate that polarization of methyl is much greater in the anions than in the cations since only about half the charge on H₃ in the latter arises from methyl polarization. The reason for this probably lies in the tendency of orbitals in anions to expand as a result of the destabilization produced by the negative charge while those in cations tend to contract. This effect should extend to parts of ions not directly carrying the formal charge. The expanded orbitals in anions should be more polarizable, and the contracted ones in cations less polarizable, than parallel orbitals in analogous neutral molecules.

E. Steric effects

The conformations of the 3-methyl and 3-ethyl anions are interesting (Fig. 2).

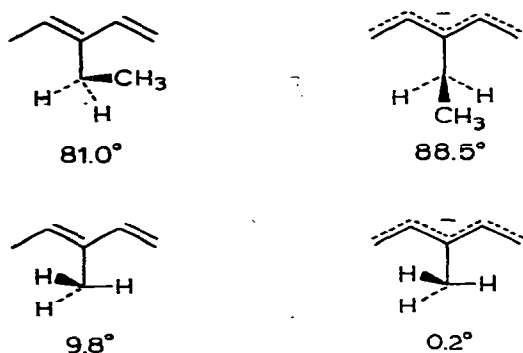


Fig. 2. Geometries of methyl- and ethyl-pentadiene and methyl- and ethyl-pentadienyl anion. Dihedral angles are given representing the smallest angle made by the C—C bond of the ethyl group or a C—H bond of the methyl group with the plane of the π -system.




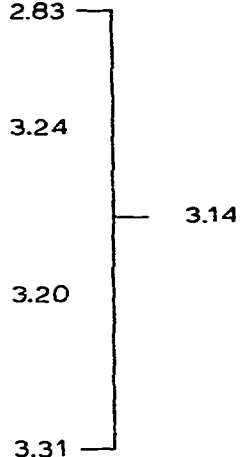
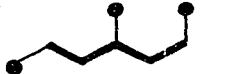
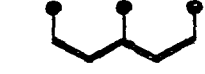

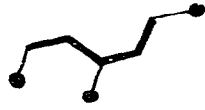

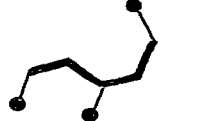
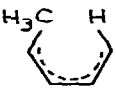

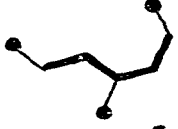
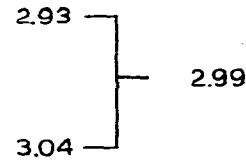
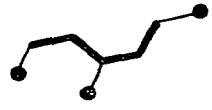
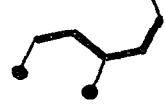
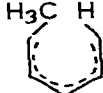
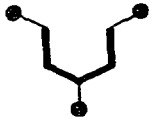

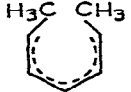
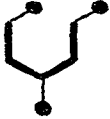

The eclipsed conformation adopted by methyl minimizes the overlap between the CH bond MOs and the $2p\pi$ AO of the adjacent carbon atom, but it also minimizes steric repulsions between the methyl hydrogen and the *cis* hydrogens at C(1) and C(2). This result would be expected if hyperconjugation is unimportant while steric effects are appreciable. We have already shown that hyperconjugation must play a negligible role in methylpentadienyl anions. Steric repulsions must on the other hand be invoked to explain the destabilizing effect of methyl at C(2) (Table 2).

The situation in 3-ethylpentadienyl cation is more ambiguous. While the symmetric conformation adopted could be due to steric repulsions, it could also indicate a significant contribution by CC hyperconjugation, this conformation maximizing the overlap of the CMe bond with the adjacent $2p\pi$ AO. Ethyl at C(3) is indeed predicted to have a marginally greater stabilizing effect on the anion than methyl (Table 2) but the difference could equally well be due to the greater polarizability of the ethyl group.

Polarization of methyl leads to stabilization of an adjacent anion by the resulting charge-dipole interactions. These should be reflected by a shortening of the corresponding $\text{CH}_3\text{—C}$ bonds. Such a contraction is indeed observed (see Table 3) in the case of the 1-methyl- and 3-methyl-pentadienyl anions, the decreases in bond length being 0.013 and 0.016 Å, respectively, i.e. greater, as expected, in the 3-position where the stabilizing effect of methyl is greater (Table 2). In the case of 2-methyl, which has a destabilizing effect, the $\text{CH}_3\text{—C}$ bond length in the anion is marginally greater (by 0.026 Å) than in the corresponding diene.

Since the stabilizing effect of methyl on pentadienyl anion seems to be due almost exclusively to polarization and since the polarization of terminal methyl C(1) or C(5) is due almost entirely to the charge on the adjacent carbon atom, it seems reasonable to suppose that the terminal *cis*- and *trans*-methyl derivatives would have identical energies, were it not for steric effects. If so, the steric energies corresponding to various situations can be estimated from the data in Table 1; Table 7 summarizes the results. These lead to the amusing conclusion that the difference in energy between the strained (*cis*) and unstrained (*trans*) isomers is almost the same (~ 3 kcal/mol) in all cases, regardless of the nature of the interfering group.

TABLE 7
STRAIN ENERGIES IN METHYLPENTADIENYL ANION

Situation	Example ^a	ΔH^b	ΔH (average)		
		vs.		2.83	
		vs.		3.24	
		vs.		3.20	
		vs.		3.31	
		vs.		2.93	
		vs.		3.04	
		vs.		2.75	
		vs.		2.82	

^a Heavy lines denote the pentadienyl system; dots denote methyl groups. ^b Difference in heat of formation in kcal/mole.

Given the induced polarity of methyl substituents in these ions, the question then arises, to what extent may the relative energies of conformers be affected by changes in the corresponding charge-dipole interactions between the methyl groups and distant carbon atoms in the pentadienyl system? Our results suggest

that the effects of such interactions should in fact be negligible, the corresponding difference between the pairs of isomers in Table 7 being ca 0.1 kcal/mol. In order to obtain further evidence concerning this, we also carried out calculations for 1-phenyl-3-methyl derivatives of the W conformer of the pentadienyl anion and for the related diene (1-phenyl-3-methylpenta-1,3-diene). The results are shown in Tables 1–4. Here the phenyl group conjugates with the pentadienyl system, leading to quite significant negative charges at the *ortho* positions. There is of course a complication in that in the *cis*-phenyl isomer, the phenyl group is twisted 30° out of the plane of the pentadienyl system through steric crowding by methyl, leading inevitably to a decrease in the conjugative stabilization of the ion by phenyl. To allow for this, we recalculated the *trans* isomer with the phenyl group twisted to an equivalent extent. The relative energies (kcal/mol) of the three isomers were (see Table 1): *trans*-phenyl (0), *trans*-phenyl (twisted) 0.81 and *cis*-phenyl 5.81. Thus the *cis*-phenyl isomer is destabilized to the extent of 5 kcal/mol by factors other than decreased conjugation. This seems surprisingly large in view of the results in Table 7, particularly those for the U conformers where comparable steric effects would be expected. Nor can the difference be attributed to electrostatic repulsion between C(3) in the pentadienyl system and the relevant *ortho* position, both of which are negatively charged, because the distance between them is almost the same in both isomers. However it is easily seen (Fig. 3) that the adjacent *ortho* position in the *cis*-phenyl derivative is nearer the negative (H(3)) end of the polarized methyl group than it is to the positive (C) one. This should lead to a net repulsion, which may well account for the unexpectedly large destabilization of the *cis* isomer.

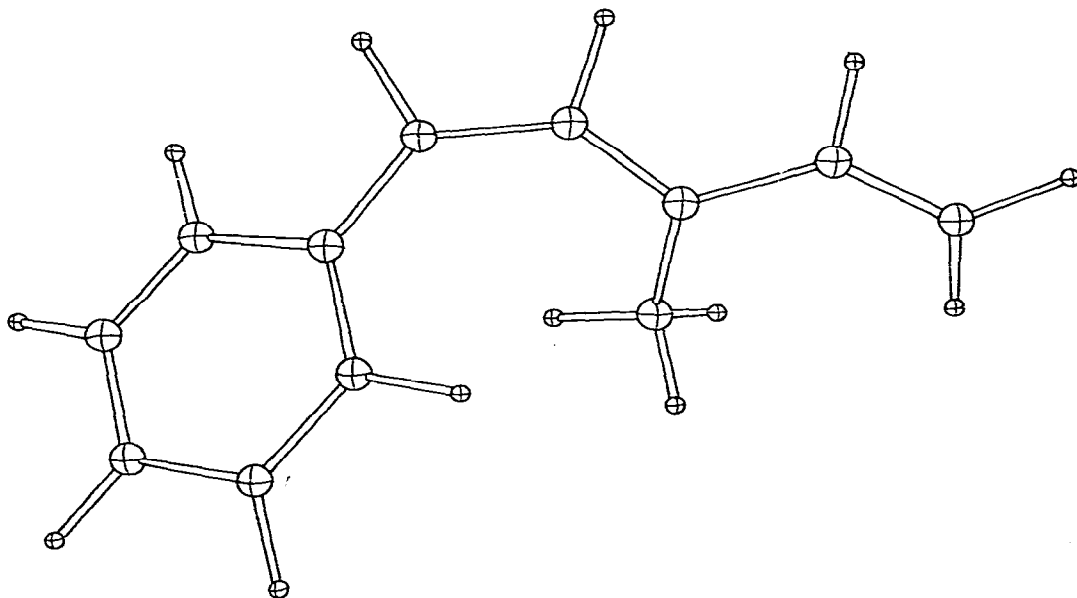


Fig. 3. ORTEP plot of *cis*-1-phenyl-3-methylpentadienyl anion.

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References

- 1 M.J.S. Dewar and W. Thiel, *J. Amer. Chem. Soc.*, **99** (1977) 4899, 4907.
- 2 (a) M.J.S. Dewar and M.L. McKee, *J. Amer. Chem. Soc.*, (1977) 5231; (b) M.J.S. Dewar and H.S. Rzepa, *ibid.*, **100** (1978) 58.
- 3 M.J.S. Dewar and H.S. Rzepa, *J. Amer. Chem. Soc.*, **100** (1978) 784.
- 4 (a) J.I. Brauman and L.K. Blair, *J. Amer. Chem. Soc.*, **92** (1970) 5986; (b) J. Hine and M. Hine, *ibid.*, **74** (1952) 5266.
- 5 J.I. Brauman and L.K. Blair, *J. Amer. Chem. Soc.*, **93** (1971) 3911.
- 6 (a) P.M.E. Lewis and R. Robinson, *Tetrahedron Lett.*, (1970) 2783; (b) W.J. Hehre and J.A. Pople, *ibid.*, (1970) 2959; (c) L.M. Jackman and D.P. Kelly, *J. Chem. Soc. B*, (1970) 102; (d) T.J. Broxton, L.W. Deedy, A.R. Katritzky, A. Lin and R.D. Topsom, *J. Amer. Chem. Soc.*, **92** (1970) 6845; (e) W.M. Schubert, R.B. Murphy, and J. Robins, *J. Org. Chem.*, **35** (1970) 951; (f) H. Kollmar and H.O. Smith, *Angew. Chem. Internat. Ed.*, **9** (1970) 462.
- 7 W.J. Hehre, R.F. Stewart and J.A. Pople, *J. Chem. Phys.* **51** (1969) 2657; (b) R. Ditchfield, W.J. Hehre and J.A. Pople, *J. Chem. Phys.*, **54** (1971) 724; (c) D.J. DeFrees, J.E. Bartmess, J.K. Kim, R.T. McIver, Jr. and W.J. Hehre, *J. Amer. Chem. Soc.*, **99** (1976) 6451; (d) A. Pross and L. Radom, *ibid.*, **100** (1978) 6572.
- 8 (a) D.W. Boerth and A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **100** (1978) 750; (b) R. Hoffman, R. Bissell and D.G. Farnum, *J. Phys. Chem.*, **73** (1969) 1789; (c) D.H. O'Brien, C.R. Russell and A.J. Hart, *Tetrahedron Lett.*, (1976) 37; (d) A. Bongini, G. Cainelli, G. Cardillo, P. Palmieri, and A. Umami-Ronchi, *J. Organometal. Chem.*, **92** (1975) C1; (e) R.J. Bushby and A.S. Patterson, *ibid.*, **132** (1977) 163; (f) D.H. O'Brien, A.J. Hart, and C.R. Russell, *J. Amer. Chem. Soc.*, **97** (1975) 4410; (g) N.D. Epitotis, *ibid.*, **95** (1973) 3087; (h) R. Hoffmann, C.C. Levin and R.A. Moss, *ibid.*, (1973) 629; (i) J.R. Grunwell and J.F. Sebastian, *Tetrahedron*, **27** (1971) 4387.
- 9 (a) J.I. Brauman and L.K. Blair, *J. Amer. Chem. Soc.*, **93** (1971) 4315; (b) R. Yamdagni and P. Kebarle, *ibid.*, **95** (1973) 4050; (c) A.H. Zimmerman, K.J. Reed and J.I. Brauman, *ibid.*, **99** (1977) 7203; (d) J.H. Richardson, L.M. Stephenson and J.I. Brauman, *J. Chem. Phys.*, **59** (1973) 5068; (e) J. Hine, *Structural Effects on Equilibria in Organic Chemistry*, Wiley, New York, 1975, p. 181.
- 10 (a) F.G. Bordwell, G.E. Drucken, G.J. McCollum, *J. Org. Chem.*, **41** (1976) 2786; (b) M. Charton, *J. Amer. Chem. Soc.*, **99** (1977) 5687; (c) J.B. Cumming and P. Kebarle, *ibid.*, **99** (1977) 5819.
- 11 R. Hoffmann and R.A. Olofson, *J. Amer. Chem. Soc.*, **88** (1966) 943.
- 12 R.B. Bates, R.H. Carnighan and C.E. Staples, *J. Amer. Chem. Soc.*, **85** (1963) 3031.
- 13 R. Gleiter, *Topics Curr. Chem.*, **63** (1976) 49.
- 14 M.P. Cooke, Jr. and R. Goswami, *J. Amer. Chem. Soc.*, **95** (1973) 7891.
- 15 (a) R.B. Bates, D.W. Gosselink, and J.A. Kaczynski, *Tetrahedron Lett.*, (1967) 205; (b) W.T. Ford and M. Newcomb, *J. Amer. Chem. Soc.*, **96** (1974) 309; (c) G.J. Heiswolf and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **86** (1967) 807; (d) G.J. Heiswolf, J.A.A. van Drunen and H. Kloosterziel, *ibid.*, **88** (1969) 1377; (e) H. Kloosterziel and J.A.A. van Drunen, *ibid.*, **89** (1970) 270; *ibid.*, **89** (1970) 368.
- 16 (a) S. Brenner and J. Klein, *Isr. J. Chem.*, **7** (1969) 735; (b) D.H. Hunter, R.E. Klinck, R.P. Steiner and J.B. Stothers, *Can. J. Chem.*, **54** (1976) 1464; (c) R.B. Bates, S. Brenner, C.M. Ccle, E.W. Davidson, G.D. Forsythe, D.A. McCombs, and A.S. Roth, *J. Amer. Chem. Soc.*, **95** (1973) 926.
- 17 (a) L.L. Corbbs and M. Hollman, *Spectrosc. Lett.*, **5** (1972) 319; (b) R.J. Bushby and A.S. Patterson, *J. Organometal. Chem.*, **132** (1977) 163.
- 18 J.F. Sebastian, B. Hsu, and J.P. Grunwell, *J. Organometal. Chem.*, **105** (1976) 1.
- 19 R.C. Bingham, M.J.S. Dewar, D.H. Lo, *J. Amer. Chem. Soc.*, **97** (1975) 1285, 1294, 1302, 1307.
- 20 (a) M.J.S. Dewar, R.C. Haddon, A. Komornicki, and H.S. Rzepa, *J. Amer. Chem. Soc.*, **99** (1977) 377; (b) M.J.S. Dewar and H.S. Rzepa, *ibid.*, **99** (1977) 7432; (c) M.J.S. Dewar and H.S. Rzepa, to be published.
- 21 M.J.S. Dewar and H. Rzepa, *J. Amer. Chem. Soc.*, **100** (1978) 777.
- 22 See M.J.S. Dewar, *Tetrahedron, Suppl.*, **8** (1966) 75.
- 23 See M.J.S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, New York, N.Y., 1969, p. 140 and section 5.5.

- 24 K.W. Egger and S.W. Benson, *J. Amer. Chem. Soc.*, **88** (1966) 241.
- 25 G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34** (1956) 523.
- 26 S.W. Benson and H.E. O'Neal, *Kinetic Data on Gas Phase Unimolecular Reactions*, NSRDS-NBS 21, U.S. Govt. Printing Office, Washington, D.C., 1970.
- 27 G.B. Ellison, P.C. Engelking, and W.C. Lineberger, *J. Amer. Chem. Soc.*, **100** (1978) 2556.
- 28 L.S. Bartell and H.K. Higginbotham, *J. Chem. Phys.*, **42** (1965) 851.
- 29 A.G. Harrison, P. Kebarle, and F.P. Lossing, *J. Amer. Chem. Soc.*, **83** (1961) 777.
- 30 The first *IP* of benzyl radical has been determined by photoelectron spectroscopy as 7.26 eV. J.M. Buschek, D. David and M.J.S. Dewar, unpublished results.
- 31 D.R. Stull, E.F. Westrum, Jr., and G.C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, John Wiley & Sons, New York, 1969.
- 32 A.H. Zimmerman and J.I. Brauman, *J. Amer. Chem. Soc.*, **99** (1977) 3565.
- 33 F.P. Lossing, *Can. J. Chem.*, **49** (1971) 357.
- 34 S. Pignataro, A. Cassuto, and F.P. Lossing, *J. Amer. Chem. Soc.*, **89** (1967) 3693.
- 35 A.H. Zimmerman, R. Gygas, and J.I. Brauman, *J. Amer. Chem. Soc.*, **100** (1978) 5595.
- 36 J.A. Kerr, *Chem. Rev.*, **66** (1965) 465.
- 37 J.H. Richardson, L.M. Stephenson and J.I. Brauman, *J. Chem. Phys.*, **63** (1975) 74.
- 38 J.L. Franklin, J.D. Dillard, H.M. Rosenstock, Y.T. Herron, K. Draxl, and F.M. Field, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand., No. 26*, 1969.