The Synthesis and Study of Pseudo-Aromatic Compounds. VII. The Analysis of the Nuclear Magnetic Resonance Spectra of 6-N,N-Dimethylaminofulvene, 1-Methyl-2-cyclopentadienylidene-1,2-dihydropyridine, and 1-Methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole[1]

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Abstract: The analysis of the nmr spectra of 6-N,N-dimethylaminofulvene, 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine, and 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole are described. Variable-temperature nmr studies of these three compounds indicate that the barriers to rotation about the C_6–nitrogen bond of 6-N,N-dimethylaminofulvene and the exocyclic double bonds of 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole and 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine are 13.5, 19.6, and 11.4 kcal, respectively.

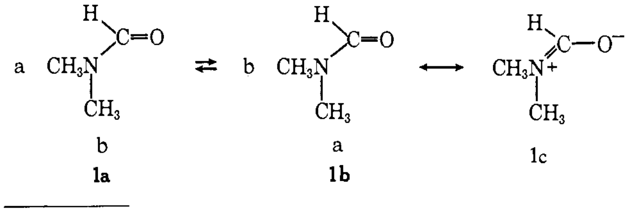
The evaluation of the importance of dipolar resonance contributors to the ground state of fulvene-type molecules is necessary for understanding these systems and to assess any π-electron delocalization energy which they might possess. The lack of an accepted criterion of π-electron delocalization severely limits any such evaluation. Thus, if aromaticity is to be characteristic of a system which possess cyclic π-electron delocalization,[3] detection of the extent of this delocalization is necessary to assess any aromatic character in substituted fulvenes.

Aromaticity can be assessed by various approaches which do not necessarily arrive at the same conclusion.[4] This property may be evaluated in terms of reactivity or lack thereof, or by π-electron delocalization as measured by diamagnetic susceptibility[5] measurements, or the observation of a ring current as measured by nmr spectroscopy.[6,7] Experience indicates that chemical reactivity is a broad spectrum with no clear-cut discontinuity which distinguishes between aromatic and nonaromatic. Therefore, these criteria are often too indefinite to be of general use.

Consideration of data such as diamagnetic susceptibility, nmr ring currents, or some other physical property dependent on π-electron delocalization will again lead to no discontinuity between aromatic and nonaromatic, but may ultimately provide a more interpretable criterion of aromatic character.[8] It appears then that it is reasonable to attempt to locate a molecule in the appropriate region of this spectrum extending from aromatic to polyolefinic by physical criteria.

An additional potentially useful method for approaching this problem would be the estimation of the relative π-bond orders in these systems. This can be done by comparison of nmr coupling constants and energy barriers to rotation about formal double bonds, when referenced to appropriate aromatic and polyolefinic models.[9]

The barrier for rotation (**1a** ⇄ **1b**) about the carbon-nitrogen bond of amides has been measured by nmr spectral methods[10] and is in agreement with data from other sources[11] which indicate that resonance structure **1c** makes a significant contribution to the ground state. Since nmr techniques are quite useful for the determination of data of this nature and are also adaptable



1a **1b** 1c

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[1] An analysis of the nmr spectrum of 6-N,N-dimethylaminofulvene has been published: H. L. Heffernan and A. J. Jones, *Australian J. Chem.*, 19, 1813 (1966). The data reported here differ from this previous report in the assignment of two hydrogens, and the coupling constants. The present work is considered to be correct on the basis that comparison of the published spectra by the above authors with the spectra in this paper (Figure 2) clearly demonstrates that the resolution in this work is significantly greater. Both our results and those of the above workers were analyzed using the method of Swalen and Reilly. However, use of Heffernan and Jones' reported parameters in our computer program predicted spectra incompatible with those experimentally obtained by us. During the preparation of this manuscript a communication appeared reporting the energy barrier for rotation about the carbon–nitrogen bond of 6-N,N-dimethylaminofulvene: A. P. Downing, W. D. Ollis, and I. O. Sutherland, *Chem. Commun.*, 143 (1967).

[2] NDEA Predoctoral Fellow, 1965–1968.

[3] W. von E. Doering and D. W. Wiley, *Tetrahedron*, 11, 183 (1860).

[4] (a) R. J. Abraham, R. C. Sheppard, W. A. Thomas, and S. Turner, *Chem. Commun.*, 43 (1965); (b) J. A. Elvidge, *ibid.*, 160 (1965).

[5] D. P. Craig, "Non-Benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, pp 24–29.

[6] J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961); G. G. Hall, A. Hardisson, and L. M. Jackman, *Tetrahedron Suppl.*, 2, 101 (1963).

[7] It appears that diamagnetic susceptibility measurements are the more sound on an experimental basis. The inability to fully evaluate the various factors which contribute to chemical shifts and thus to the determination of the presence and extent of a ring current in nmr spectra make this method less reliable.

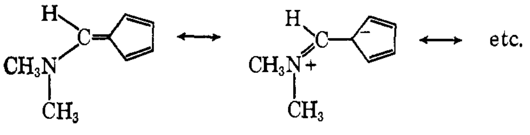
[8] Although we essentially agree with the viewpoint of Elvidge,[4b] the difficulty in evaluating the various contributors to chemical shifts prohibits the general use of estimating ring currents as a criterion of aromatic character.

[9] (a) N. Jonathan, S. Gordon, and B. P. Bailey, *J. Chem. Phys.*, **36**, 2433 (1962); (b) W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Am. Chem. Soc.*, **89**, 1438 (1967); (c) W. B. Smith and B. A. Shoulders, *ibid.*, **86**, 3118 (1964); (d) A. S. Kende, P. T. Izzo, and P. T. MacGregor, *ibid.*, **88**, 3559 (1966).

[10] W. D. Phillips, *J. Chem. Phys.*, 23, 1363 (1955); M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).

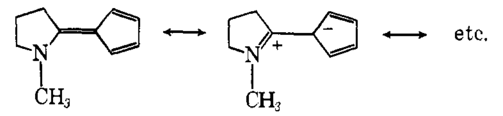
[11] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p 207.

for studying reactive compounds, this method should prove useful in studying pseudo-aromatic compounds. For example, 6-N,N-dimethylaminofulvene (**2**) can be considered a derivative of N,N-dimethylformamide in which the carbonyl has been replaced by a cyclopentadienylidene system. Determination of the barrier for rotation about the fulvene C_6–nitrogen bond should then serve as a basis for estimating the contribution of the dipolar resonance structure **2b**. Modification of



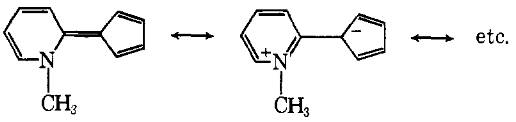
2a **2b**

the basic structure of this aminofulvene to that of 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole (**3**) would then enable the determination of the barrier to rotation about the fulvene C_5–C_6 double bond



3a **3b**

in this system.[12] Again, this measurement should be an indication of the importance of dipolar resonance contributors to the ground state of a 6-aminofulvene π system. The combined knowledge of these two parameters should be a reliable indication of the property being studied. An additional system, 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine[13] (**4**), was also investigated in this study since this system possesses a potential aromatic stabilization of the positive charge developed from dipolar resonance contributor **4b**. Also the data provided by this study should complement the available dipole moment data for this system and 6-N,N-dimethylaminofulvene.[13]



4a **4b**

1-Methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole (**3**) was synthesized by a sequence analogous to that of 6-N,N-dimethylaminofulvene.[14] The salt derived from dimethyl sulfate and N-methyl-2-pyrrolidone condensed readily with sodium cyclopentadienide to give **3**. The structure was confirmed by the nmr spectrum (Figure 1) which was completely consistent with that assigned.

Results and Discussion

The nmr spectra (Figures 1 and 2) of these three compounds studied were quite solvent dependent, which caused the relative chemical shifts to vary significantly in different solvents. The coupling constants for the compounds were determined by computer techniques using the method of Swalen and Reilly,[15] and are listed in Table I (see also Figures 1 and 2). It is immediately apparent from the nmr spectra of 6-N,N-dimethylaminofulvene that the methyl groups are rapidly equilibrating at ambient temperature on the nmr time scale. Also the observed ABCD spectrum for the five-membered ring indicates that at ambient temperature rotation about the fulvene double bond is slow on the nmr time scale. It is equally apparent from the observed AA′BB′ spectrum for the five-membered ring of 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine that this ring is rapidly rotating on the nmr time scale at ambient temperature. The observed ABCD nmr spectrum for the cyclopentadienylidene ring in 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole indicates that at ambient temperature the fulvene ring is not rapidly rotating on the nmr time scale. However, since the temperature at which such equilibration occurs is a consequence of $\Delta\nu$ between the hydrogens if rotation were not occurring, as well as the bond energies, no conclusions can be drawn on only ambient temperature spectra.

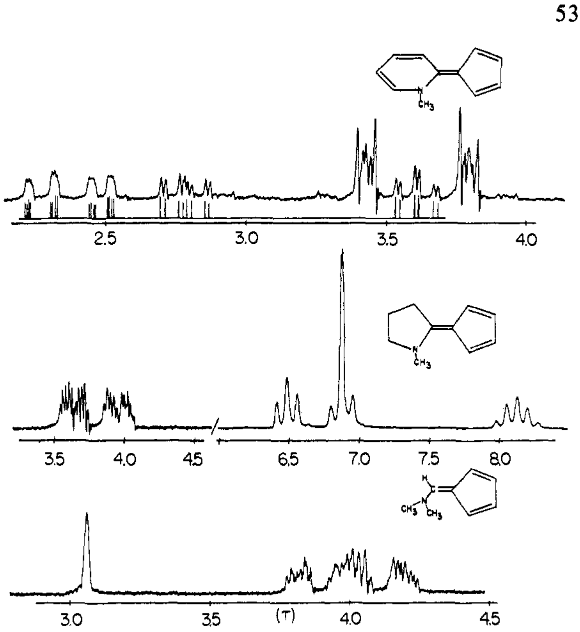


Figure 1. The nmr spectra of 6-N,N-dimethylaminofulvene (in acetone), 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole (vinyl region in acetonitrile, aliphatic region in deuteriochloroform), and 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (in acetonitrile) with TMS as an internal reference.

Heating solutions of 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole caused the observed ambient temperature ABCD spectrum to coalesce to an AA′BB′ spectrum in the nmr (Figure 3). This change in the nmr spectrum is consistent with the interpretation that at higher temperatures the rate of rotation of the five-membered ring about the fulvene double bond becomes rapid on the nmr time scale. Similar experiments with 6-N,N-dimethylaminofulvene exhibit a similar temperature dependence (Figure 3) except that complete coalescence could not be observed at the temperature accessible.[16] In addition, cooling solutions

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[12] Although these data are also available directly from 6-N,N-dimethyl aminofulvene, experimental difficulties make 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole a useful model compound, as is discussed below.

[13] J. A. Berson, E. M. Eveleth, Jr., and Z. Hamlet, *J. Am. Chem. Soc.*, **87**, 2887 (1965); J. A. Berson, E. M. Eveleth, Jr., and S. L. Mannat, *ibid.*, **87**, 2901, 2908 (1965).

[14] K. Hafner, K. H. Voepel, G. Ploss, and C. Koenig, *Ann.*, **661**, 52 (1963).

[15] J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

[16] The highest attainable temperature with dimethylacetamide in a sealed tube was 175°. Above this temperature boiling of the solvent prevented any spectral determinations. As can be seen in Figure 2, the data are sufficient to determine the activation parameters in spite of

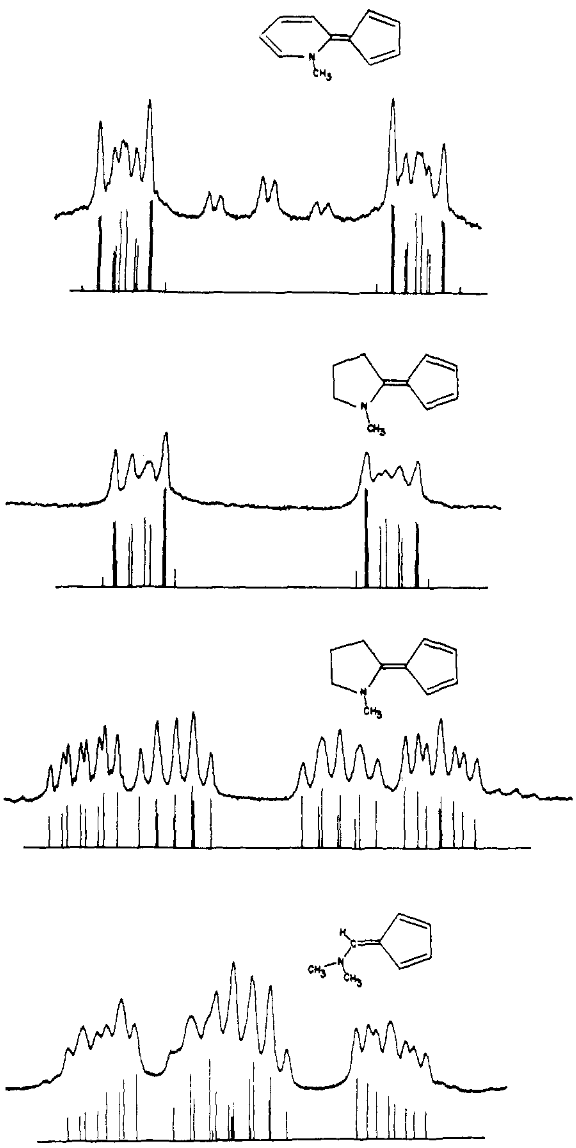

Figure 2. High-resolution and calculated nmr spectra of the cyclopentadienylidene ring of 6-N,N-dimethylaminofulvene, 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole (0°), this same compound at 150°, and 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine.

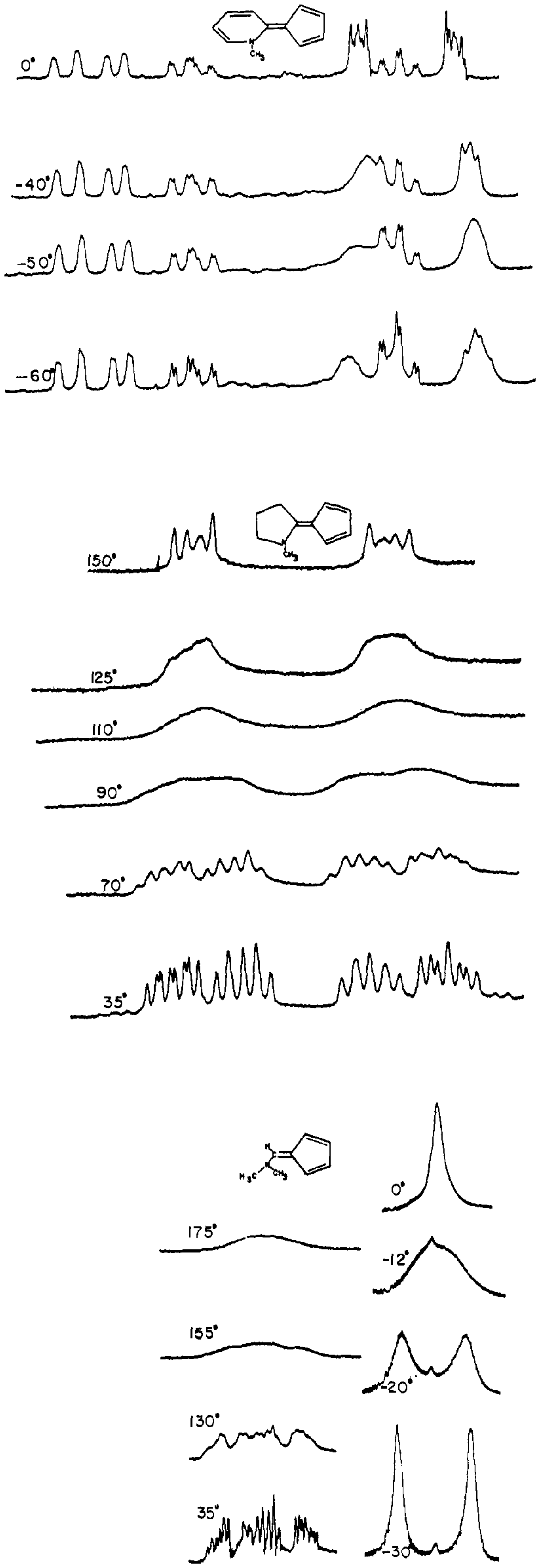

Figure 3. Typical coalescence nmr spectra of 6-N,N-dimethylaminofulvene, 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole, and 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine.

of 6-N,N-dimethylaminofulvene and observation of the nmr spectrum indicated that at low temperatures the ambient temperature single peak observed for the methyl groups splits into two separate absorptions. Finally, similar low-temperature nmr studies on 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine indicated that the ambient temperature AA'BB' spectrum for the five-membered ring separated into an ABCD pattern (Figure 3), although it could not be well resolved due to solubility difficulties at low temperatures. From the data obtained from these experiments the activation energies for the various rotational barriers were calculated employing the usual assumptions,[17] and are listed in Table II.

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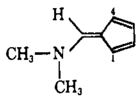
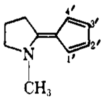
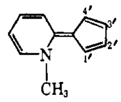
these experimental difficulties. The data derived from 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole are assumed to be more reliable, although the difference is not sufficiently great to affect the present discussion.

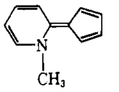
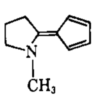
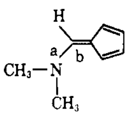
(17) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance," Pergamon Press Inc., London, 1965, pp 550–560. The activation parameters determined are somewhat solvent dependent, but the error introduced by this factor is too small to be significant in the present discussion (see Table II). A combination of solubility and boiling point difficulties prevented using the same solvent throughout.

Table I. Nmr Parameters

Compound	Chemical shifts,[a] τ	Coupling constants,[a,b] cps	Solvent	Temp, °C
	H_1 3.82	$J_{1.2}$ 4.73	$CH_3CON(CH_3)_2$ (0.5 *m*)	37
	H_2 3.97	$J_{1,3}$ 1.46		
	H_3 4.20	$J_{1.4}$ 2.17		
	H_4 4.03	$J_{2.3}$ 2.52		
	H_6 3.06	$J_{2.4}$ 1.96		
	H_7 6.98	$J_{3.4}$ 4.56		
	H_3 6.50	$J_{1',2'}$ 4.60	$CH_3CON(CH_3)_2$ (0.5 *m*)	30
	H_4 8.09	$J_{1',3'}$ 1.57		
	H_5 6.90	$J_{1',4'}$ 2.20		
	$H_{1'}$ 3.60	$J_{2'.3'}$ 2.64		
	$H_{2'}$ 3.90	$J_{3',4'}$ 4.50		
	$H_{3'}$ 4.03	$J_{2'.4'}$ 1.99		
	$H_{4'}$ 3.70	$J_{4.5}$ 7.5		
	CH_3 6.87	$J_{3.4}$ 7.2		
	H_3 . . .	$J_{1'.2'}$ 5.02[c]	$CH_3CON(CH_3)_2$	130
	H_4 . . .	$J_{1'.3'}$ 1.18		
	H_5 . . .	$J_{1'.4'}$ 1.03		
	$H_{1'}$ 3.65	$J_{2'.3'}$ 2.64		
	$H_{2'}$ 3.96	$J_{3'.4'}$ 5.02		
	$H_{3'}$ 3.96	$J_{2'.4'}$ 1.18		
	$H_{4'}$ 3.65			
	CH_3 . . .			
	H_3 2.27	$J_{3.4}$ 9.30	CH_3COCH_3 (0.5 *m*)	37
	H_4 2.79	$J_{3.5}$ 1.50		
	H_5 3.61	$J_{4.5}$ 6.50		
	H_6 2.48	$J_{4.6}$ 1.60		
	$H_{1'}$ 3.43	$J_{5.6}$ 6.50		
	$H_{2'}$ 3.79	$J_{1'.2'}$ 4.51		
	$H_{3'}$ 3.79	$J_{1'.3'}$ 1.78		
	$H_{4'}$ 3.43	$J_{1'.4'}$ 2.26		
	CH_3 6.14	$J_{2'.3'}$ 2.54		
		$J_{2'.4'}$ 1.78		
		$J_{3'.4'}$ 4.51		

[a] The data do not allow an unequivocal assignment of the five-membered ring hydrogens. Thus the alternate numbering scheme derived by rotating the five-membered ring 180° without changing the number of the various carbon atoms cannot be excluded. [b] The coupling constants are assumed to be accurate to ±0.2 cps. [c] Loss of resolution does not permit as accurate an assignment of coupling constants for the coalesced form.

Table II. Activation Energy Parameters

Compound	Solvent	Δν AB, cps	T_c, °C	E_a, kcal
	0.5 *m* acetone	16.5	−50	11.4
	0.5 *m* acetone	11.5	100	19.6
	1.0 *m* acetonitrile	10.6	75	18.3
	20% w/w dimethylacetamide	11.3	90	19.1
	a 0.5 *m* acetone-d_6	11.7	−12	13.5
	20% w/w acetonitrile	4.0	−17	13.8
	20% w/w dichloromethane	3.3	−22.5	13.6
	20% w/w chloroform	1.9	−40	11.8
	b 0.5 *m* dimethylacetamide	21.0	~150	~21.9

In three cases studied, the most reasonable transition state is assumed to be approximated by the perpendicular conformation, involving a charge-separated species rather than a diradical species. The data of Table II indicate that 6-N,N-dimethylaminofulvene exhibits a measurable (13.5 kcal) energy barrier to rotation about the carbon–nitrogen bond. This barrier must be a consequence of a significant contribution from dipolar resonance forms such as **2b**, and the observed activation energy is a measure of the loss of carbon–nitrogen π bonding in the transition state for rotation.[18] The relatively low barrier[19] to rotation about the exocyclic

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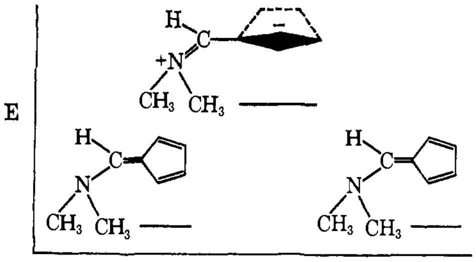
(18) This conclusion is emphasized by the fact that the observed energy barrier is that for breaking the π bond between the nitrogen and carbon 6 of the fulvene ring.

(19) The experimental energy barriers for rotation about the ethylenic double bonds of stilbene is 42.8 kcal and for *p,p'*-N,N-dimethylaminonitrostilbene is 17.1 kcal.[20] However, in this case it is less evident how the various contributions to the ground state and transition state for rotation should be assigned.

(20) M. Calvin and H. W. Alter, *J. Chem. Phys.*, **19**, 768 (1951).



carbon–carbon double bond of 6-N,N-dimethylaminofulvene (21.9 kcal) and 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole (19.6 kcal) is in agreement with the same conclusion. Also consistent with this interpretation is the even lower observed activation energy for rotation (11.4 kcal) of the five-membered ring in 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine. The interpretation that the ground states are essentially homopolar and that the low activation parameters for compounds **3** and **4** are due almost entirely to stabilization of the transition states is excluded by the above discussion. These data and conclusions are consistent with that proposed from the dipole moment data for compounds **2** and **4**[13] and in fact appear to indicate a somewhat greater contribution from dipolar character than would be predicted from the dipole moment data alone.

At this point it is important to consider the remaining nmr data. The analysis of the coupling constants and chemical shifts of the six-membered ring of 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine is also pertinent to understanding these systems. The hydrogen assignments for this molecule were arrived at by the following considerations. The two low-field doublets at τ 2.27 and 2.48 in the nmr spectrum of this compound must be due to the 3- and 6-hydrogens of the pyridine ring. The doublet at τ 2.27 is assigned to the 6-hydrogen on the basis that under high resolution this doublet shows less fine structure than the one at τ 2.48. This observation is consistent with a quadrupole interaction of the 6-hydrogen with the nitrogen atom causing line broadening. Based on this assumption the remaining assignments (Table I) for the six-membered ring hydrogens are determined by the observed coupling constants. The unusual chemical shift of the 5-hydrogen is consistent with the various valence bond structures of the resonance hybrid, none of which place a positive charge at carbon 5. This same consideration would also predict that the 3-hydrogen should also appear at approximately the same chemical shift as the 5-hydrogen. However, the anisotropy of the double bonds of the cyclopentadienylidene ring would be expected to cause a significant downfield shift of the 3-hydrogen.

It has been pointed out that a relationship between vicinal coupling constants and bond orders has a theoretical justification.[9b] It appears reasonable that nmr coupling constants are related to π-electron delocalization in that both are related to bond order. For this reason comparison of the coupling constants for the cyclopentadienylidene ring of the molecules studied here with cyclopentadiene can lead to a qualitative estimate of π-electron delocalization. The coupling constants for cyclopentadiene are $J_{1,2}$ = 5.06 cps and $J_{2,3}$ = 1.94 cps.[21] Assuming that in a completely delocalized five-membered ring the coupling constants would converge to an average of *ca.* 3.5 cps,[9] the cyclopentadienylidene ring in the compounds studied here indicate some enhancement of π-electron delocalization. Thus, the coupling constant across the formal single bond has increased *ca.* 30% toward the difference between cyclopentadiene and the average value, and the coupling constants across the formal double bonds have decreased in a similar manner.

The coupling constant data are also consistent with pronounced double bond–single bond character in these molecules, as predicted by molecular orbital calculations.[13] Therefore, the present data indicate that the molecules studied here exhibit limited cyclic π-electron delocalization. Considering the electrostatic work which is necessary to separate the charge in resonance structures[22] such as **2b**, **3b**, and **4b**, it is logical that these resonance structures will not contribute to the resonance hybrid on an equal basis with **2a**, **3a**, and **4a**. Therefore, qualitatively the ground-state wave functions will be a hybrid of these various structures with the **a** components making the major contribution. For this reason it appears that the **a** structures are the best single valence bond representations of these systems. The consequence of this latter effect will be that the nmr spectra will be more characteristic of polyolefinic compounds rather than aromatic compounds in spite of significant π-electron mobility.

The difference in the activation energies for rotation of the five-membered ring in 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole and 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine also reflects these same considerations. The dipole moments of 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (5.1 D.) and 6-N,N-dimethylaminofulvene (4.5 D.) are quite similar. These data indicate that the pyridinium contribution in the ground state of **4** does not significantly enhance the dipolar character over that of N,N-dimethylaminofulvene.

Based on the assumption that one can treat the dipole moment of N,N-dimethylaminofulvene as the separation of point charges from the center of the five-membered ring to the nitrogen,[23] and doing the appropriate geometrical calculations, the observed dipole moment is caused by a separation of charge of 1.33 esu over the indicated distance. Calculation of the distance from the center of the five-membered ring to the center of the six-membered ring of 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine and multiplying by the same charge separation (*i.e.*, 1.33 esu) gives a predicted dipole moment of 5.13 D. Therefore, qualitatively, the amount of dipolar character is not significantly enhanced by including the nitrogen of an aminofulvene into a pyridinium π system. This same conclusion is reflected in the nmr coupling constants.

Thus the relatively lower activation energy for rotation of the five-membered ring in 1-methyl-2-cyclo-

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(21) S. L. Manatt and D. D. Elleman, as quoted by J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3896 (1965).

(22) R. B. Turner, W. R. Meador, W. von E. Doering, J. R. Mayer, and D. W. Wiley, *ibid.*, **79**, 4127 (1957); R. B. Turner, "Theoretical Organic Chemistry," Butterworth & Co. (Publishers) Ltd., London, 1959, pp 68–70.

(23) Although this assumption is an oversimplification, the errors introduced in the discussion should be somewhat self-consistent and not invalidate the conclusions drawn. This calculation is based on a regular pentagon for the five-membered ring and a regular hexagon for the six-membered ring. However, again the errors introduced will not effect the qualitative conclusions drawn.

pentadienylidene-1,2-dihydropyridine compared to that for 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole is interpreted to reflect a more significant pyridinium resonance contribution to the transition state than to the ground state. It might be anticipated that the transition state for this process in 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine should be approximately the resonance energy of pyridine lower than that for 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole. The observed difference in activation energies for these two systems (8.2 kcal) indicates that in the transition state the expected additional pyridinium resonance stabilization is not fully realized because energetically it is partially lost as additional electrostatic work necessary to separate a greater amount of charge over a greater distance.

Experimental Section

All nmr spectra were determined on a Varian Model HA-100 spectrometer equipped with a variable-temperature probe. The computations were performed on an IBM Model 360/50 computer. The carbon and hydrogen analysis was performed by Galbraith Laboratories Inc., Knoxville, Tenn.

1-Methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole (3). Cyclopentadiene (13.3 g, 0.2 mole) was added dropwise with stirring to a suspension of sodium hydride (4.8 g, 0.2 mole) in 50 ml of tetrahydrofuran, under nitrogen. A mixture of N-methyl-2-pyrrolidone (19.8 g, 0.2 mole) and dimethyl sulfate (25.2 g, 0.2 mole) was heated for 20 min on a steam bath. The resulting complex was added dropwise to the sodium cyclopentadienide solution which was cooled to −5° in an ice–salt bath. After the resulting mixture had stirred *ca.* 2 hr, the suspension was filtered, and the resulting brown solution was concentrated on a rotary evaporator. This yielded a brown oil which solidified on cooling. This material was recrystallized two times from cyclohexane to give pale yellow needles (14.0 g, 50%) of 1-methyl-2-cyclopentadienylidene-2,3,4,5-tetrahydropyrrole (mp 100–101°). Carbon and hydrogen analyses were consistent with the molecular formula.

The remaining two compounds were prepared by methods reported in the literature and exhibited physical properties consistent with those reported.

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Crowded Benzenes. VI.[1] The Strain Energy in *o*-Di-*t*-Butylbenzenes[2]

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Abstract: The standard strain energy, ΔH_{strain}, of *o*-di-*t*-butylbenzene (ODTB) is defined as the difference in standard heat of formation of this compound and its *para* or *meta* isomer (PDTB or MDTB). On the basis of the following evidence, ΔH_{strain} for this system is found to be 22.3 ± 0.5 kcal/mole, which is close to Brown's estimate. ODTB is converted rapidly and exothermically by aluminum bromide in carbon disulfide to a variety of products whose number and nature depend on [$AlBr_3$]. PDTB or MDTB yields the same array of products as ODTB (or products of equivalent heat of formation) under the same conditions. When the calorimetrically determined heats of reaction are corrected for heats of solution in CS_2 alone, their difference may be related directly to ΔH_{strain} in the gas phase because the heats of vaporization and complexing with aluminum bromide are nearly equal for liquid, unstrained, isomeric dialkylbenzenes. Even though the heats of reaction and product yields for both isomers are sensitive to [$AlBr_3$], over 37 products being formed at the highest concentration, the *difference* between their heats of reaction is invariant to conditions. This indicates that there is a single large energy difference between them and this we equate to ΔH_{strain}. ΔH_{strain} for 1,2,4-tri-*t*-butylbenzene (TTB) (relative to 1,3,5-TTB) is estimated in the same way to be 22.3 ± 1 kcal/mole. This value is reconciled with a previous estimate by a correction for heat of sublimation. Furthermore, mass spectral comparisons of (P − 15) appearance and ionization potentials for ODTB *vs.* PDTB or MDTB and of 1,2,4-TTB *vs.* 1,3,5-TTB indicate an energy difference of about 20 kcal/mole. ΔH_{strain} is more than half the usually accepted resonance energy of benzene. However, there is no evidence from nmr, infrared, or electronic spectra or from the reactions of compounds containing the *o*-di-*t*-butylbenzene system that a "nonaromatic benzene" has been produced by warping the ring. The only indication for loss of aromatic character is a 30% decrease (relative to benzene) in Dauben's diamagnetic susceptibility exaltation.

Over a decade ago, Brown and his students[4–7] deduced by their method of homomorphic analogy that aromatic compounds carrying two *t*-butyl groups in an *ortho* arrangement should be destabilized by strain energy amounting to at least 25 kcal/mole. The pos-

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[1] For previous paper in this series, see E. M. Arnett, J. M. Bollinger, and J. C. Sanda, *J. Am. Chem. Soc.*, 87, 2050 (1965). Requests for reprints should be sent to E. M. A.

[2] Presented in preliminary form at the Benzene Centennial Symposium on Aromatic Character and Resonance, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965. Most of the material in this paper is taken from the thesis of J. C. Sanda, University of Pittsburgh, 1966.

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