Nitrogen Analogs of Sesquifulvalene. II. Theoretical Correlation of Ground-State Properties[1a,2]

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The dipole moments of a series of nitrogen anhydro bases and pyridones can be calculated by a modified Hückel technique. The agreement with experimental values is quite good. Despite pronounced bond alternation, the conjugated systems of the anhydro bases have substantial charge separation as evidenced by experimental dipole moments, a result that is not predicted by considerations of n.m.r. chemical shifts. The relative acidities of the conjugate acids of these substances are not properly predicted by Hückel theory, probably because of the undue emphasis the calculation places on formal conjugation. The large spread in acidities in the series cyclopentadiene, indene, and fluorene is drastically compressed by attachment of a pyridinium nucleus. Much of the effect of annelation of the five-membered ring on the acidities of the anhydro bases of the 2-series seems to be attributable to intramolecular overcrowding in the annelated derivatives, which produces noncoplanarity of the conjugated system.
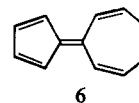
As a test of the predictive and correlative power of the Hückel molecular orbital (HMO) method,[3] we have carried out calculations of the π-electron energy levels, bond orders, and charge densities for a number of nitrogen analogs of sesquifulvalene (6)[4] and for several related compounds. The calculations provide the framework for an examination of the utility and limitations of simple HMO theory and some of its variants in accounting for the observed[2] chemical and physical properties of these substances. The results bear on problems associated with predictions of "aromaticity" in conjugated π-electron systems and on what observables are to be taken as appropriate measures of that elusive and ill-defined property.

6

Ground-State Properties. Dipole Moments. When the calculated value of a physical property is strongly dependent on the accuracy of the wave functions, as is the case with dipole moments, the HMO method frequently must be modified. The exaggeratedly high calculated π-electron moments that usually result from the overemphasis that the simple Hückel procedure gives to charge separation[3] sometimes can be at least partially compensated by the ω-technique[3b,5] supplemented in the case of heteroatom systems by a judicious choice of parameter values in the assignment of Coulomb integrals to the heteroatoms and of resonance integrals to the bonds of the π-electron system. Although the resulting wave functions suffer from a complaint common to those derived from "approximate" MO methods in that often they do not serve well for the description of other properties, they nevertheless have correlative value.

In Table I are listed the calculated and observed dipole moments for two of the simple anhydro bases of our series (9 and 13), and those of five closely related substances 43, 47, 48, 79, and 80, as well as the observed values for three analogs 49, 50, and

| 8, R=CH_3 | 13, R = CH_3 | 43 |
| 9, R = CH_2C_6H_5 | 14, R=CH_2C_6H_5 | |

47   48
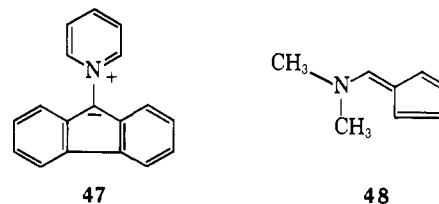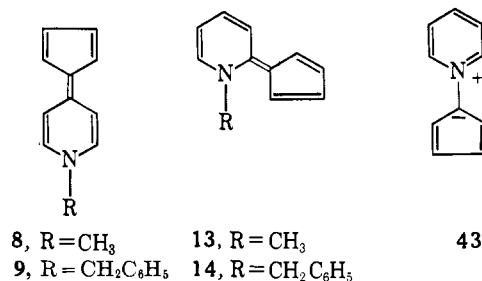
51 in which the cyclopentadienyl residue has been replaced by oxygen. The method of calculation (essentially the ω-technique) and the choices of values for the parameters h_x and k used in the matrix elements ($\alpha_x = \alpha_0 + h_x\beta_0$ and $\beta_{rs} = k\beta_0$) are described in detail in the Appendix, but we note here the highly salutary

(5) G. W. Wheland and D. E. Mann, J. Chem. Phys., 17, 264 (1949).

Table I. Calculated[a] and Observed Dipole Moments

Compd.	μ, D. Calcd.[a] A	Calcd.[b] B	Obsd.
1-Methyl-2-cyclopent-adienylidene-1,2-di-hydropyridine (13)	9.8	7.9	5.1[c]
1-Benzyl-4-cyclopent-adienylidene-1,4-di-hydropyridine (9)	12.9	10.5	9.7,[d] 8.9[c]
Pyridinium cyclopent-adienide (43)[g]	12.6	13.6	13.5[e,f]
Pyridinium fluore-nylide (47)[h]	..	14.0	4.1[i]
6-Dimethylamino-fulvene (48)[j]	..	4.5	4.5[k]
1-Methyl-2-pyridone (49)	4.0	4.0	4.15[l]
1-Methyl-4-pyridone (50)	6.7	6.4	6.9[l]
Pyridine N-oxide (51)	..	4.32, 5.26[m]	4.18[n]
2-Methyl-2-pyrindine (79)	..	5.6	o
1-Methyl-1-pyrindine (80)	..	4.9	p
Pyrrocoline (84)	..	1.7	q

[a] Without initial bond alternation (see Appendix). [b] With initial bond alternation (see Appendix). [c] W. D. Kumler, J. Org. Chem., 28, 1731 (1963). [d] D. N. Kursanov, M. E. Vol'pin, and Z. N. Parnes, Khim. Nauka i Promy., 3, 159, 1958; Chem. Abstr., 52, 20108i (1958). [e] M. E. Volpin, Russ. Chem. Rev. (English Transl.) 29, 129 (1960). [f] D. N. Kursanov and N. K. Baranetskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. (English Transl.), 341 (1958). [g] D. Lloyd and N. S. Sneezum, Chem. Ind. (London), 1221 (1955). [h] F. Kröhnke, Angew. Chem., 65, 605 (1953). [i] Reference 6. [j] H. Meerwein, W. Florian, N. Schön, and G. Stopp, Ann., 641, 1 (1961). [k] K. Hafner, K. H. Vöpel, G. Ploss, and C. König, ibid., 661, 52 (1963). [l] A. Albert and J. N. Phillips, J. Chem. Soc., 1294 (1956). [m] Did not converge after 24 cycles of iteration. Values shown are those of the 8th and 9th cycles, which approached convergence more closely than any other vicinal pair. [n] A. N. Sharpe and S. J. Walker, J. Chem. Soc., 4522 (1961). [o] Not measured. For preparation of 2-phenyl-2-pyrindine, see A. G. Anderson, Jr., W. F. Harrison, R. G. Anderson, and A. G. Osborne, J. Am. Chem. Soc., 81, 1255 (1959); A. G. Anderson, Jr., W. F. Harrison, and R. G. Anderson, ibid., 85, 3448 (1963). [p] Not measured. For preparation, see C. B. Reese, ibid., 84, 3978 (1962). [q] Not measured. For preparation, see V. Boekelheide and R. J. Windgassen, Jr., ibid., 81, 1456 (1959); V. Boekelheide and W. Feely, J. Org. Chem., 22, 589 (1957).

effect of taking bond-length alternation explicitly into account by variations of k. The electron density distributions derived by this procedure give a much better approximation of the observed dipole moments


49   50   51   79   80
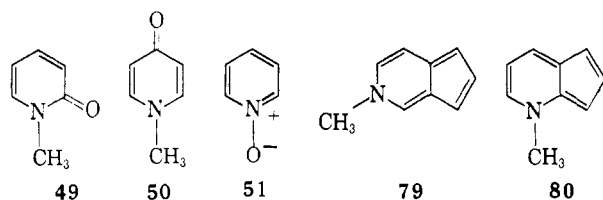
(Table I) than do those using the assumption that β_{rs} is invariant. The simple Hückel calculation can be improved, even with all β_{rs} initially equal, by a modified ω-technique (calculation A of Table I) in which not only charge densities but also bond orders are recycled to self-consistency; however, the best results are obtained by varying the initial β_{rs} values (calculation B of Table I). As is outlined in more detail in the Appendix, calculation B uses the charge

density distribution from each cycle as input data for the matrix elements in the next cycle of iteration, but the initially assigned β_{rs} values are used throughout. The charge density distributions for all the cases except pyridine N-oxide (51) converge to constancy in both calculations.

The calculations assign the negative end of the dipole to the five-membered ring in the anhydro bases 13 and 9 and in the fulvene 48. The polarity calculated for the other cases of Table I is in accord with that expected on electrostatic grounds. With the exception of the case of pyridinium fluorenylide 47, for which the experimental value was obtained[6] with an impure sample, the calculated π-electron moments correspond remarkably well to the observed total moments; the largest discrepancy occurs in the case of 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (13), where the calculated value is too high by about 55%. The agreement emphasizes the extreme importance of introducing bond alternation explicitly into the calculation. (For example, the calculated moment for 8 is 17.6 D. by the simple Hückel treatment.) The generally successful correlation suggests that the calculated values of the dipole moments of the two azulene analogs 79 and 80 (see Table I) should be matched rather well when measured experimentally.

The small σ-bond moment is not included in the calculation. This contribution would have the effect of weakly counteracting the π-moment, since in most of the cases the electronegative nitrogen atom would induce electron displacements in the direction opposite to that associated with the π-moment. The σ-moment may well make a substantial contribution to the total moment of pyrrocoline (84), since the calculated π-moment is small.

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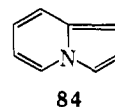
The recent measurements of Kumler[7] confirm the previous conclusion[8] that 1-benzyl-4-cyclopentadienylidene-1,4-dihydropyridine (9) has an exceptionally high dipole moment; this corresponds to about 25–30% contribution of a zwitterionic structure to the resonance hybrid.[7] About the same relative zwitterionic contribution accounts for the observed[7] dipole moment of 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (13). These moments are even higher than those of the corresponding pyridones 49 and 50 (Table I). Although it is difficult to give an accurate estimate of the σ-moments that would be expected for compounds 9 and 13, it seems likely that they would not exceed 1–2 D.,[9] and in any case would oppose the π-moment. The large observed total moment thus implies a rather substantial electronic delocalization. This conclusion is contrary to that deduced[10] from studies[11] of the nuclear magnetic resonance (n.m.r.)

(6) H. Hartmann and H. Grossel, Z. Elektrochem., 61, 337 (1957).
(7) See Table I, footnote c.
(8) See Table I, footnote d.
(9) For a discussion of such estimates, see R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, Chapter IX.
(10) G. V. Boyd and L. M. Jackman, J. Chem. Soc., 548 (1963).
(11) Cf. G. G. Hall, A. Hardisson, and L. M. Jackman, Tetrahedron Suppl., 2, 101 (1963).

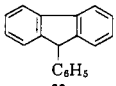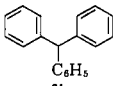**Table II.** Calculated Acidity Measures (Δm) of Some Phenyl-Substituted Hydrocarbons

Hydrocarbon	E_π, β-units	Anion	Anion (ω)	Δm,[a] β-units	$1 + \Delta m$,[b] β-units
C_6H_5 **55**	12.932	14.872	12.984	1.940	1.052
C_6H_5 **56**	12.857	14.872	12.984	2.015	1.127
C_6H_5 **57**	12.606	14.872	12.984	2.276	1.378
C_6H_5 **58**	18.815[c]	20.598	18.564	1.783	0.749
C_6H_5 **59**	18.424[e]	20.598	18.564	2.174	1.140
C_6H_5 **60**	24.293[d]	26.363	24.141	2.080	0.848
C_6H_5 **61**	24.000	22.200		1.800[e]	. . .

[a] Hückel calculation. [b] ω-calculation. [c] B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson et Cie, Paris, 1952, p. 226. [d] A. Streitwieser, Document No. 6222, ADI Auxiliary Publications Project, Library of Congress, Washington, D. C. [e] Reference 18b.

spectra of 1-butyl-4-cyclopentadienylidene-1,4-dihydropyridine and **13**. The proposal[12] that the n.m.r. chemical shift of ring and side-chain protons is a *quantitative* measure of "aromaticity," coupled with the observed values of chemical shifts in such substances as **9** ($CH_2C_6H_5 = (CH_2)_3CH_3$),[11] **13**,[11] and **52**,[13] is interpreted[10,13] as indicating that the homopolar

52   **53**   **54**
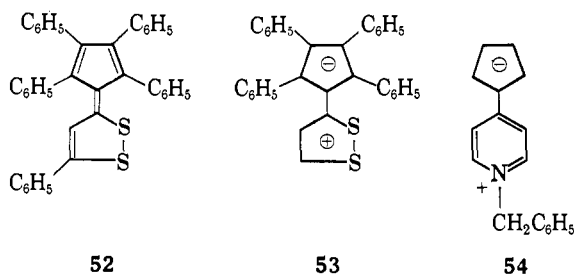
structures are adequate representations of these molecules and that there is relatively little electron delocalization and charge separation such as would result from important contributions of heteropolar structures like **53** and **54**. Regardless of the general validity or inadequacy of this criterion of "aromaticity," compound **9** has one of the highest dipole moments ($\mu = $ ca. 9 D.) recorded for a substance that is not a formal zwitterion (compare, for example, p-nitrodimethylaniline, $\mu = 6.87$ D.[14]); it would seem difficult in these

circumstances to support the view that the contribution of the dipolar structure **54** is "unimportant." Further, the connection between n.m.r. chemical shifts and charge separation or electron delocalization is clearly not yet on a sufficiently precise basis[15] to allow a prediction of either from a knowledge of the other. If the charge separation in sesquifulvalene itself (**6**) turns out to be as low as that calculated ($\mu = 2.19$ D.) by a self-consistent MO method,[16] the heterocycles **8** and **13** will be "analogs" of **6** in structure but not in properties.

Dissociation of the Conjugate Acids. The rather rough values for the acid dissociation constants of the hydrocarbon series cyclopentadiene $>$ indene $>$ fluorene $>$ diphenylmethane[17] are correlated satisfactorily by simple Hückel molecular orbital (HMO) theory.[18] The dissociation constant is a function of the difference, ΔE, in HMO π-electron energy between the anion A and the conjugate acid AH. In eq. 1,[18] α is the carbon coulomb integral and β is the resonance integral. The term Δm, the difference in bonding

(12) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961).

(13) A. Lüttringhaus, E. Futterer, and H. Prinzbach, *Tetrahedron Letters*, 1209 (1963).

(14) L. G. Wesson, "Tables of Electric Dipole Moments," The Technology Press, Massachusetts Institute of Technology, Cambridge, Mass., 1948.

(15) For previous discussions of such relationships, see *inter alia* (a) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838, 1846 (1961); (b) H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961); (c) A. Streitwieser, Jr., A. Heller, and M. Feldman, *J. Phys. Chem.*, **68**, 1224 (1964); (d) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5816 (1960). For a discussion of ring currents in some heterocyclic compounds, see (e) R. J. Abraham, R. C. Sheppard, W. A. Thomas, and S. Turner, *Chem. Commun.*, **43** (1965).

(16) A. J. Silvestri, L. Goodman, and J. A. Dixon, *J. Chem. Phys.*, **36**, 148 (1962).

(17) (a) W. K. McEwen, *J. Am. Chem. Soc.*, **58**, 1124 (1936); (b) J. B. Conant and G. W. Wheland, *ibid.*, **54**, 1212 (1932).

(18) (a) G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1935); (b) A. Streitwieser, Jr., *Tetrahedron Letters*, **6**, 23 (1960).

Table III. Calculated Acidity Measures and Observed pK_a Values of Some Pyridinium (Py) Compounds

Compd.	Conj. base	Δm_p	Δm_H	Δm_ω + 1	pK_a
62	8	2.324	1.001	1.215	...
63	8	2.073	0.669	0.881	8.87–9.17[b]
64	8	1.998	0.613	0.824	8.87–9.17[b]
65	33	2.255	0.913	1.134	8.66–8.96[b]
66	33	1.864	0.544	0.833	8.66–8.96[b]
67	24a	2.186	0.885	1.078	10.03
68		1.646	0.502	0.989	12.1
76	43	...	...	1.475	
77	43	...	...	1.267	10.0[d]
78	43	...	...	1.233	
69	13	2.332	1.018	1.231	...
70	13	2.081	0.676	0.899	8.37[f]
71	13	2.006	0.617	0.829	8.70[g]
72	32	2.262	0.883	1.147	10.95–11.25[b]
73	32	1.871	0.551	0.846	10.95–11.25[b]
74	23	2.182	0.821	1.089	11.72
7S		1.646	−0.530	0.995	12.5

[a] 4Py = 1-methyl-4-pyridinium. [b] See text. [c] 1Py = 1-pyridiinum. [d] E. M. Kosower and B. C. Ramsey, *J. Am. Chem. Soc.*, **81**, 856 (1959). It is not known which of the cations **76, 77,** or **78** predominates. [e] 2Py = 1-methyl-2-pyridinium. [f] Or 8.70. [g] Or 8.37.

energy coefficients for the two systems, is a measure of acidity, and (to the approximation[18] that ΔE can be equated to ΔF of dissociation and that variations

$$\Delta E = (E_\pi)_A - (E_\pi)_{AH} = 2\alpha + \Delta m\beta \qquad (1)$$

in solvation in the series can be neglected) should be linearly related to $-pK_a$, i.e., the more acidic substances should have larger Δm values.

The conjugate acids of our anhydro bases are pyridinium-substituted cyclopentadienes, indenes, and fluorenes. Experimental values for the acidities of the analogous all-carbon systems, i.e., phenylcyclopentadiene, phenylindene, and phenylfluorene, are not available, but a predicted order of acidities can be calculated by the above technique. These calculations illustrate some new complications that are not present in calculations on the parent hydrocarbons (cyclopentadiene, indene, fluorene) and that have direct analogies in the nitrogen systems. The results for the hydrocarbon acids given in Table II are derived from the usual Hückel assumptions[3] with neglect of overlap.

The effect of annelation in the phenyl-substituted series can be assessed by comparing appropriate members. In such comparisons, the ability of phenylcyclopentadienide and phenylindenide anions to accept a proton at more than one site and hence to afford more than one conjugate acid must be kept in mind. Thus, appropriately chosen series should involve annelation as the sole structural variable. For example, the series 57, 58, and 60 is inappropriate because 58 is not related to 57 by annelation. The two proper series derivable from the data of Table II are 56, 58 and 57, 59, and 60. In both series, the effect of annelation is predicted to be acid weakening, just as in the unsubstituted series. A further prediction from the results is that the most highly conjugated acid of a given annelation level will be the weakest one, i.e., the acidities in the cyclopentadiene series will fall in the order 57 > 56 > 55, and the indene series, 59 > 58. This would also be predicted from qualitative resonance considerations combined with the fact that the acids in each series give common conjugate anions.[19] The acid-strengthening effect of the cyclopentadiene residue is reflected in the comparison of 9-phenylfluorene (60) with triphenylmethane (61).

The series of pyridinium-substituted acids for which experimental data are available from our previous work[2] are listed in Table III together with Δm values calculated for these and a number of related molecules. Since in the pyridinium cases more than one conjugate acid is formed, we can no longer restrict our correlation to the direct annelation effect (as we do above for the hypothetical phenyl cases). The Δm values of Table III are derived from three separate calculations of increasing "refinement."

(1) The quantity Δm_p is the energy change calculated by a first-order perturbation of the direct Hückel energy levels of the phenyl-substituted compounds of Table II. In this approximation, the π-electron energy

(19) The above discussion ignores a symmetry effect,[20] which in the ionization of cyclopentadiene, for example, would require the observed pK_a to be diminished by an amount log 5, as well as smaller corrections of this type in other cases. The corrections are all much smaller than the experimental error in currently available acidity measurements on these compounds.
(20) S. W. Benson, J. Am. Chem. Soc., 80, 5151 (1958).

E_1 of the perturbed system that results from replacing CH by $^+$NR (thus converting phenyl to pyridinium) is related to E_0, the corresponding energy for the unperturbed model, by eq. 2

$$E_1 = E_0 + q_r\Delta\alpha_r \qquad (2)$$

where q_r is the π-electron charge at atom r and $\Delta\alpha_r$ is the change in Coulomb integral at atom r by which the system is perturbed.[21] For the calculation of the Δm_p values of Table III, $\Delta\alpha_r$ is taken to be 2.00 β.

(2) Calculations by a modified simple Hückel method give the values Δm_H. In the customary notation, the Coulomb integral of the nitrogen is given as $\alpha_N = \alpha_C + h_N\beta_0$, where α_C is the carbon Coulomb integral, β_0 is the standard "aromatic" resonance integral, and h_N is a parameter. In some cases, certain bonds are assigned resonance integrals parametrically modified as $\beta_{rs} = k\beta_0$ to accommodate anticipated alternations in bond length. A list of h and k parameters for the calculations is given in the Appendix.

(3) The values $\Delta m_\omega + 1$ are derived from energies calculated by the modified ω-technique[4,5] described above. In each case, the eigenvalues converge after several iterations (see Appendix), and the results probably represent a more realistic picture of the charge distribution than that given by method 2, as judged by the dipole moment results.

The Δm_H and Δm_ω values differ from the corresponding Δm_p values by roughly 1 and 2 β-units, respectively. These are fictional discrepancies arising from the treatment of the anhydro bases as true zwitterions in the perturbation treatment and from the differences in "core" energies between the simple Hückel and ω-techniques. More significant is the fact that the spread of Δm values becomes compressed as the method of calculation is refined. The range is 0.686β between 68 and 69 by the perturbation technique (method 1) and falls to 0.516β in the Hückel calculation (method 2) and to 0.407β in the ω-calculation (method 3).

The calculations of Table III again predict that annelation will be acid weakening in both the 2- and 4-series for those cases where comparisons are permissible (62 > 65 > 67; 63 > 66; 69 > 72 > 74; 70 > 73). In correlating the experimental data, however, the comparisons involve other groupings. In the 2-series, for example, the two parent acids are 70 and 71,[2] with the next higher annelation stages being 73 (and possibly 72) and then 74. In the cases of the cyclopentadienyl acids 70 and 71, the pK_a values are precisely known,[2] but the weaker indenylidene acid (presumably 73) could have a pK_a as much as log 2 pK_a units lower than the apparent value of 11.25.[2] The range of values is given in Table III. On the assumption that the other indenyl acid 72 is very much stronger than 73, the observed apparent pK_a refers only to the weaker acid. If this is the case, the correlation breaks down, because 73 is predicted by each method of calculation to be a weaker acid than the fluorenyl analog 74 and by the ω-technique, even weaker than the benzhydryl analog 75, in conflict with experiment. (The comparisons are given graphically in Figures 1 and 2.) Similar difficulties occur in the 4-series, where

(21) (a) C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London), A191, 39 (1947); (b) ref. 3, p. 111; (c) ref. 9, p. 80.
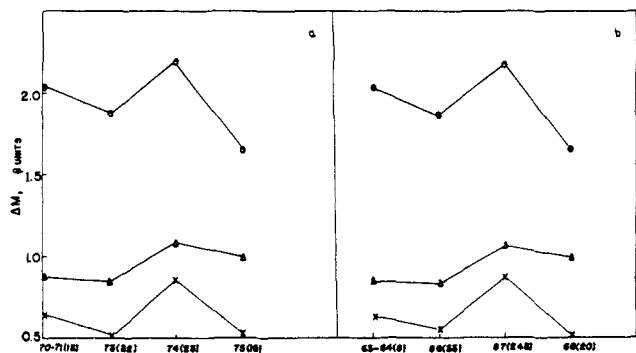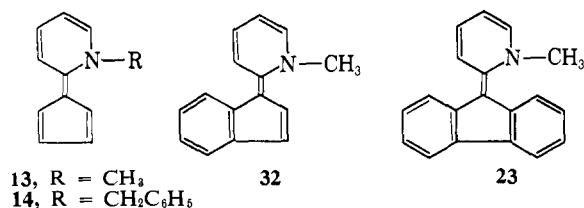
Figure 1. Calculated Δm-values as a function of structure for the 2-series and the 4-series. The 70-71 and 63-64 values are averages: $\bigcirc$, Δm_p; $\times$, Δm_H; $\triangle$, $\Delta m_\omega + 1$. The numbers in parentheses along the abscissa refer to the conjugate bases. The sequence from left to right is cyclopentadienyl, indenyl, fluorenyl, and benzhydryl.
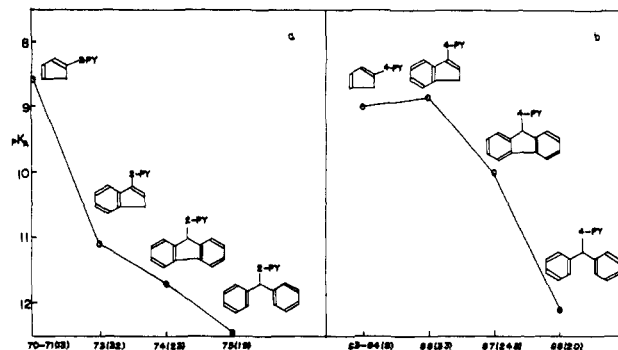

Figure 2. Experimental pK_a values. The 70-71 and 63-64 values are averages. The numbers in parentheses along the abscissa refer to the conjugate bases. The sequence from left to right is cyclopentadienyl, indenyl, fluorenyl, and benzhydryl.

although the Hückel technique correctly predicts the benzhydryl analog 68 to be the weakest acid of the series, the indenyl compound 66 is out of line with 63, 64, and 67. The ω-technique predicts the wrong order for 68 and 66. Similarly, the cyclopentadienyl acids in which the pyridinium ring is conjugated with one or two double bonds 63, 64, 70, and 71 are predicted to be weaker than the fluorenyl acids 67 and 74. These apparent anomalies probably reflect the overemphasis that the MO method places on delocalization energy.[22] The extra conjugation of the pyridinium ring with the double bond in the weaker acids of the indenyl and cyclopentadienyl derivatives leads to an exaggeratedly large estimate of the delocalization energy by the MO calculations and consequently to an underestimate of the Δm value.

Although the calculations of Table III correctly predict that the unconjugated cyclopentadienyl acids 62 and 69 of both the 2- and 4-series should be stronger than the fluorenyl analogs,[23] there is a serious theoretical problem associated with steric hindrance to planarity in the anhydro bases of the 2-series. This increases in the order 13 < 32 < 23, the distortion in the last member of the series, 23, being so severe that a Stuart–Briegleb model cannot be constructed with an internuclear double bond. It seems quite likely, therefore, that 23 (and possibly also 32) are nonplanar molecules, whereas all the MO calculations are done on the assumption of planarity. Thus, it is not clear what portion

13, R = CH₃
14, R = CH₂C₆H₅

32   23

of the observed acidity effects must be ascribed to quantum mechanical causes of the kind treated in the MO calculations and what portion to differing degrees of deviation from planarity in the members of the series. Qualitatively, however, it seems likely that the steric

difficulties in 23 (and to a lesser extent in 32) would act in such a way as to reinforce the quantum mechanical annelation effect. In the acids of all three members of the series, the conjugation is disrupted so that there is no longer a formal internuclear double bond,[2] and consequently there is much smaller need for coplanarity. In the conjugate bases, however, the requirement is restored, and the difficulty of meeting it in the hindered cases 32 and 23 would result in smaller π-electron stabilization energies for these bases than the MO calculation would suggest. The effect would be to make the calculated Δm values too high for the dissociations of 32 and 23 conjugate acids, with the discrepancy being bigger in the case of 23. Thus, the acidities along the series 13, 32, and 23 would descend more steeply than would be the case if the steric factor were absent. In this connection we note that whereas there is a 1000-fold range of acidities in the 2-series 13, 32, and 23, the range in the 4-series 15, 33, and 24a, where the steric effect is absent, is compressed to about a power of ten (see Figure 2). This would suggest that at least a large part, if not the major part, of the effect of annelation in the 2-series is exerted by the increased twisting about the internuclear bond that results from increased steric requirements as benzo rings are fused onto 13.

A rough estimate of the severity of this twisting can be made with the help of the assumptions[24–26] embodied in eq. 3, where β is the resonance integral for the

$$\beta = \beta_0 \cos \theta \qquad (3)$$

twisted internuclear bond, β_0 is the standard resonance integral, and θ is the dihedral single of twist. If it is assumed that in the acids, which have no formal internuclear double bond, the variation of the internuclear β with twist can be neglected, then to a first approximation the effect of the twisting is felt only in the anhydro bases, where the twisted compound will be π-electronically less stable than the planar one by an amount given by eq. 4.

$$\delta E = p_{rs}\beta_0(\cos \theta - 1) \qquad (4)$$

(22) M. J. S. Dewar and H. N. Schmeising, Tetrahedron, 11, 96 (1960).

(23) The unconjugated acid 69 is not formed when 13 is protonated.[2] Consequently, 69 must be a stronger acid than either 70 or 71, both of which are formed and both of which are stronger than 74. Thus 69 is stronger than 74.

(24) (a) Cf. ref. 3, p. 16; (b) cf. J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, New York, N. Y., 1961, p. 82.

(25) Cf. C. A. Coulson in "Steric Effects in Conjugated Systems," Academic Press Inc., New York, N. Y., 1958, p. 8.

(26) (a) R. G. Parr and B. L. Crawford, J. Chem. Phys., 16, 526 (1948); (b) M. J. S. Dewar, J. Am. Chem. Soc., 74, 3345 (1952).

The quantity p_{rs} is the mobile bond order for the internuclear bond.

The observed 100-fold greater range of acidities in the 2-series as compared to the 4-series corresponds to an energy effect of about 3 kcal./mole. If this is due entirely to twisting, the angle of deformation can be calculated from eq. 4 and the MO quantities p_{rs} and β_0. The mobile bond order p_{rs} for the internuclear bond has an average value of about 0.64 for the members of the 2- and 4-series, and the quantity β_0 may be estimated to be about -35 to -49 kcal./mole. The values for β_0 are taken from the most recent[27] correlations of hydrocarbon acidities, and although originally used[27] for reactions in which a neutral acid gives an anionic conjugate base, are here assumed to apply also to proton dissociations of cationic acids to neutral bases. Fortunately, θ is not extremely sensitive to uncertainties in β_0 in the range used, so that the assumption could be quite crude without greatly affecting the value of θ.[28] From eq. 4, θ is 25–29°. The calculation is subject to some question, however, since although the largest decrease in acidity in the 2-series comes with the change 13 → 32, models suggest that the largest twist should come in the next stage of annelation, 32 → 23.

The effect of a pyridinium substituent on the acidity of a cyclopentadiene derivative is very large. Both the 2- and 4-cyclopentadienylpyridinium cations (70, 71, 63, and 64) are stronger acids than cyclopentadiene itself (pK_a ∼ 14[27]) by about five powers of ten. These substances are even stronger acids than 1-pyridinium cyclopentadiene cation[29] (pK_a ∼ 10), despite the concentration of positive charge much closer to the site of dissociation in the latter. Much of the driving force for the greater acidity of the cations of the 2- and 4-series must derive from the extra conjugation energy in the corresponding anhydro bases.

Annelation of cyclopentadiene to indene and thence to fluorene produces an experimental range of acidities tentatively estimated as covering 17 powers of ten.[27] Mere substitution of a 4-pyridinium group in this series causes a dramatic compression of the range to about one power of ten (Table III). The effect, although superficially startling, is quite reasonable. Thus, in the hypothetical series of 4-pyridinium derivatives 62, 65, and 67, where the structural change is true annelation, Δm changes by about 0.11–0.14 β-unit, depending upon the method of calculation (Table III), whereas in the series cyclopentadiene, indene, fluorene,[18b] Δm changes by 0.48 β-unit. If β is the same for both series, therefore, the acidities of the pyridinium compounds should cover only four or five powers of ten instead of 17.[30]

A still further compression would result from the circumstance that the acids 62 and 65 are so strong relative to their isomers 63/64 and 66 that their pK_a values cannot be measured by our techniques. Thus, the ex-

perimental values we have refer to a series in which the range should be even narrower than the four to five pK_a units predicted for the hypothetical series. In principle, it should be possible to account for the remaining discrepancy of three to four pK_a units in terms of the difference in acidity between the strongest acid of the hypothetical series (62) and the observed value for the 63/64 pair. For the reasons already discussed, the theoretical estimate of this discrepancy will be too large because of the exaggerated importance the calculation attaches to delocalization energy in 63 and 64. Since the hydrocarbon acidity scale is presently only tentative,[27] it does not seem fruitful to attempt to push the analysis further than the demonstration just given that the apparently enormous energy compression can be rationalized readily.[31]

Appendix

The MO calculations were facilitated by the use of a matrix diagonalization program and subroutines for the IBM 7090 digital computer. The program was written to give MO quantities (eigenvalues, bond orders, free valence indices, and charge densities) directly.

The E_π values for the *hydrocarbon series* (Table II) were obtained by the usual Hückel technique with neglect of overlap, i.e., $S_{ij} = 0$ for $i \neq j$; $S_{ij} = 1$ for $i = j$. All the resonance integrals between adjacent atoms were assigned unit values; those between nonadjacent atoms were assigned the value zero.

The quantities Δm_p (Table III) were determined, as described in the text, by first-order perturbation calculations on the results of Table II.

The quantities Δm_H (Table III) were obtained from calculations using parametrically modified matrix elements in the Hückel secular determinant. The nitrogen Coulomb integral was taken as $\alpha_N = \alpha_C + h_N\beta_0$, and the resonance integral' was evaluated as $\beta_{rs} = k\beta_0$; h_N was set equal to 1.50, and k-values are listed below.

The quantities Δm_ω (Table III) were determined by a modification of the ω-technique. Parameter values for the first cycle are listed below. The calculations were reiterated with new Coulomb parameters for the $(N + 1)$th cycle computed from $\alpha_i = \alpha_i^0 + 1.4(n - q_i)\beta_0$, where q_i is the computed charge density at atom i for the Nth cycle, β_0 is the standard resonance integral, and n is the number of core charges contributed by atom i ($n = 1$ for carbon and oxygen and 2 for nitrogen). The calculations were recycled until no q_i value changed by more than 0.001 unit. Convergence was expedited by averaging the q_i-values for the $(N - 1)$th and $(N - 2)$th cycle and using the averaged[32] value for the Nth cycle. In this way, the charge distributions converged in about seven to ten iterations, although occasionally as many as 13 or 14 were required. These charge density distributions were used to compute the calculated dipole moments given in Table I.

(27) A. Streitwieser, W. C. Langworthy, and J. I. Brauman, *J. Am. Chem. Soc.*, 85, 1761 (1963).

(28) For further justification of β_0 values in this range, see R. Breslow and H. W. Chang, *ibid.*, 83, 2367 (1961), who take $\beta_0 = 32$ kcal./mole for pK_{R^+} values of triarylcyclopropenium ions; ref. 3, p. 364–367, and references therein cited, where values of -42 kcal./mole and *ca.* -30 kcal./mole are used for other ionization equilibria in which cations are produced.

(29) See Table III, footnote *d*.

(30) A similar but somewhat smaller compression is predicted for the phenyl-substituted series 57, 59, and 60 (Table II).

(31) Since this paper was first submitted, the hydrocarbon acidity scale has been compressed [E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, 87, 382 (1965); A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *ibid.*, 87, 384 (1965)], and the presently proposed range is only about 8 or 9 powers of ten instead of 17. On this basis the correlation in the pyridinium series becomes quite good, since the annelation affect is now predicted to produce an acidity range of about 100, which is within an order of magnitude of that observed.

(32) *Cf.* R. Ettinger, *Tetrahedron*, 20, 1579 (1964).

For the list of parameters, the pyridine ring is numbered in conventional fashion. The five-membered ring present in most of the compounds is numbered by calling A the carbon atom through which attachment is made to the heterocyclic ring. The two carbon atoms of the five-membered ring attached to A are both called B, and the two attached to B (and to each other) are called C. For example
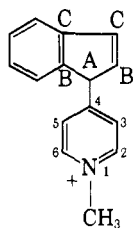
For the *pyridinium conjugate acids* (**62–78**) the following parameters were used in the Hückel and ω-calculations: $h_N = 1.50$; h for C_2 and C_6 of the pyridine ring $= 0.40$; all other h-values $= 0.00$. For all the resonance integrals of the pyridinium ring, k was taken as 1.00; for the internuclear bond (*i.e.*, C_2–A C_4–A) in the conjugate acids of the anhydro bases, $k = 0.90$; for formally single bonds A–B, B–C, or C–C, $k = 0.90$; for formally double bonds A–B, $k = 1.06$. In all others, $k = 1\,00$. For the internuclear bond (*i.e.*, N–A) in the conjugate acid of pyridinium cyclopentadienide (**76, 77,** and **78**), $k = 0.75$.

For the bases, $k = 1.06$ for all formal carbon–carbon double bonds, 0.90 for carbon–carbon single bonds, 0.75 for carbon–nitrogen single bonds, and 1.00 for carbon–nitrogen double bonds. The aromatic carbon–carbon double bonds in benzo rings and all the bonds in the five-membered ring of pyridinium cyclopentadienide (**43**) were given $k = 1.00$. For the oxygen compounds **49** and **50**, $h_0 = 1.00$; k for the carbon–oxygen double bond $= 1.00$; all other parameters were assigned as in the case of the anhydro bases.

Dipole moments (Table I) were calculated as vector sums from the charge distributions obtained from the ω-calculations and a molecular geometry assigned with reference to reasonably analogous substances of known geometry. Since the moments are not very sensitive to small changes in geometry, the precise values used are not reproduced here. The ω-calculations (A) themselves were carried out with all initial $\beta_{rs} = \beta_0$, *i.e.*, with $k = 1$. The off-diagonal elements of the secular determinant in the Nth cycle were given by the equation[33]

$$\log \beta_{rs} = \log \beta_0 + 0.224 p_{ij} - 0.149$$

where p_{ij} is the bond order between atoms r and s in the $(N - 1)$th cycle. The modifying terms vanish (*i.e.*, $\beta_{rs} = \beta_0$) when p_{ij} has the benzene π-bond order 0.667. About seven or eight cycles were required for convergence. Calculation B was carried out as described above for the results of Table III.

(33) *Cf.* H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* (London), A251, 172 (1959).

Nitrogen Analogs of Sesquifulvalene. III. Theoretical Correlation of Excited-State Properties[1a,2]

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The experimental energies and intensities of the electronic absorption bands of a series of nitrogen analogs of sesquifulvalene are compared with the results of three kinds of theoretical treatment. Although the Hückel theory and its variant, the ω-method, are satisfactory in correlating much of the data, they fail to account for the major observed difference in behavior between the members of the 2- and 4-series, namely, the occurrence of two strong, long wave length bands in the 2-series but of only one in the 4-series. Treatment of the data by first-order perturbation theory, using the series of anions phenylcyclopentadienide, phenylindenide, and phenylfluorenide, gives better results. The transition energies are correlated with the values calculated from perturbation theory with a correlation coefficient of 0.953; the value of the resonance integral β, obtained from the slope of the correlation, is -47.6 kcal./mole.

In the preceding paper of this series,[2b] we presented a correlation of molecular orbital theory with some of the experimentally determined[2a] ground-state properties