TABLE II

COUPLING CONSTANTS OF METHYL β-D-THIAXYLOPYRANOSIDE (C.P.S.)

$J_{1a,2a}$	8.4
$J_{2a,3a}$	8.6
$J_{3a,4a}$	8.6
$J_{4a,5e}$	3.3
$J_{4a,5a}$	11.2
$J_{5a,5e}$	13.5

C-2 and C-4 protons with J values of 8.6, which confirms the axial–axial relation between C-2 and C-3 protons and further indicates that the C-3 proton is in axial–axial orientation with the C-4 proton.

The two quartets in the region 7.0–7.7 τ are assigned to the C-5 protons. This is due to the coupling among themselves and with the neighboring proton at C-4. Part of the splitting pattern of the C-4 proton is overlapped by the signals due to the C-2 proton and the methyl hydrogens. This is treated as an ABX-type[11] spectrum, and the values of the various coupling constants which can be deduced from these spectral features are summarized in Table II. The large coupling constant $J_{5e}J_{5a}$ is expected for the interaction of axial and equatorial protons on the same carbon atom.[9] The small J value for the coupling of the equatorial proton on C-5 with the proton on C-4, and the corresponding large value for the coupling of the axial proton on C-5 with this same proton, show beyond a doubt that the proton on C-4 is in an axial orientation.

In summary, the n.m.r. spectra show no evidence for any important alterations in ring conformation due to the replacement of the ring oxygen of D-xylopyranose by sulfur. Furthermore, the spectra of methyl β-D-thiaxylopyranoside are in accord with the Cl ring conformation.

Acknowledgment.—We are indebted to the Corn Industries Research Foundation for financial support of this work.

[11] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chap. 6.

Dipole Moments of Two Nitrogen Analogs of Sesquifulvalene

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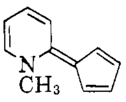
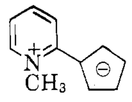
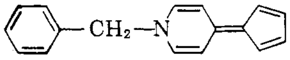
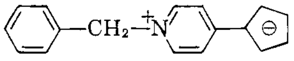
The dipole moments of 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (I) and 1-benzyl-4-cyclopentadienylidene-1,4-dihydropyridine (II) are of interest because of possible large contributions of resonance forms with a separation of charge, Ia and IIa, which would cause these molecules to have large dipole moments.[1-5]


I


Ia


II


IIa

The moment of compound I has not been reported and although that of II has been reported to be 9.7 D.,[1] no experimental details were given. If the electronic polarization was calculated from atomic refraction constants, the reported moment would be high because of the likely exaltation in such a compound.

Results and Discussion

The results are given in Table I. Compound I was sufficiently soluble so solutions up to the usual concentration range of about 1% could be measured and in this range the ϵ_{12}–ω_2 points still fell on a straight line giving no evidence of association. The $P_{E_{20}}$ from the refractive index of the solutions was about 22 units higher than the MR$_D$ value, indicating considerable exaltation as expected from this type of compound. The dipole moment of 5.20 ± 0.6 D. gives evidence of approximately a 25% contribution from the forms with a separation of charge Ia and IIa. This calculation was made without taking into account the small moment possessed by the normal forms I and II of the compound since the direction of this small moment is not known with regard to the resultant moment coming mainly from the contribution of the forms with a separation of charge.

Since the solubility of compound II was less than 10 mg. in 10 ml. of benzene, only very dilute solutions could be measured. The density of these solutions was indistinguishable from that of benzene, but dielectric constant differences were significant. More concen-

TABLE I

DIPOLE MOMENTS IN BENZENE AT 25°

1-METHYL-2-CYCLOPENTADIENYLIDENE-1,2-DIHYDROPYRIDINE

ω_2	ϵ_{12}	ν_{12}
0.0	2.2725	1.14025
.0021995	2.3156	1.13935
.0046113	2.3593	1.13830
.0074636	2.4168	1.13726
.0102930	2.4702	1.13636
.0127364	2.5301	1.13532

ϵ_1 = 2.2702 α = 19.9269 ν_1 = 1.14017

β = −0.38057 P_{2_0} = 3.96391 P_{2_0} = 623.205

$P_{E_{20}}$ = 69.70 from refractive index of solutions

MR$_D$ = 47.75

μ = 5.20 ± 0.06 D.

1-BENZYL-4-CYCLOPENTADIENYLIDENE-1,4-DIHYDROPYRIDINE

ω_2	ϵ_{12}	ν_{12}
0.0	2.2756	1.141947
.00012881	2.2792	1.141947
.00028457	2.2859	1.141947
.00058901	2.2975	1.141947

ϵ_1 = 2.2750 α = 37.9034 ν_1 = 1.14195

β = 0.0 P_{2_0} = 7.4455 P_{2_0} = 1736.97

$P_{E_{20}}$ = 108.57 from refractive index of solutions

MR$_D$ = 70.07

μ = 8.93 ± 0.18 D.

[1] D. N. Kursanov, M. E. Vol'pin, and Z. N. Parnes, *Khim. Nauka i Promy.*, **3**, 159–73(1958); *Chem. Abstr.*, **52**, 20108i (1958).

[2] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[3] D. N. Kursanov and N. K. Baranetskaya, *Bull. Acad. Sci. USSR*, 341 (1958).

[4] G. V. Boyd, *Proc. Chem. Soc.*, 263 (1960).

[5] J. A. Berson, E. M. Evleth, and Z. Hamlet, *J. Am. Chem. Soc.*, **82**, 3793 (1960).

trated solutions could be made in dioxane, but these were so hygroscopic that it was difficult to get meaningful measurements since in the instrument used some exposure of the solution to the air was unavoidable. The dipole moment of 8.9 ± 0.2 D. was obtained from the three most dilute solutions in benzene. These three points and the one for the solvent fell on a straight line, but the next point at $\omega_2 = 0.00088499$ fell considerably below the line and the next more concentrated solution precipitated slightly and was still further off the line. It is evident that association begins beyond a concentration of about 6 mg. in 10 ml. in this case. The dipole moment calculated from the dioxane solutions came out 8.1 D., but this is probably not so accurate as the value from the benzene solutions. The value of 8.9 D. is smaller than the value of 9.7 D. obtained by the previous workers and this might, in part, be accounted for if they calculated the MRD value from tables. There is no doubt, however, that this molecule has a high moment. The value of 8.9 D. indicates that there is a contribution of about 27% from forms with a separation of charge, again no account being taken of the moment present in the normal form of the molecule. This is about the same as the contribution of the forms with a separation of charge in compound I.

Experimental

The dielectric constants were measured using a Dipolmeter Model DM 01. The dipole moments were calculated using the method and equation of Halverstadt and Kumler.[2] The dioxane was purified by refluxing with about one-hundredth of its volume of concentrated hydrochloric acid with an exit tube from the reflux condenser leading outdoors, neutralizing and drying with solid potassium hydroxide, refluxing over sodium, and fractionally distilling twice from sodium through a 30-plate column.

Thiophene-free benzene was refluxed over sodium wire and then fractionally distilled from a 30-plate column.

Compound I,[5] orange needles, had m.p. 74–75°; compound II,[3,6] golden yellow plates, decomposed above 200°. The infrared and ultraviolet-visible spectra of these substances were identical with those reported.[3,5,6]

Acknowledgment.—The author wishes to thank Dr. Jerome Berson for suggesting the measurements be made and for supplying pure samples[5,6] of the compounds, and Mr. Thomas Simpson, Jr., for programming the calculations on the 1620 IBM computer.

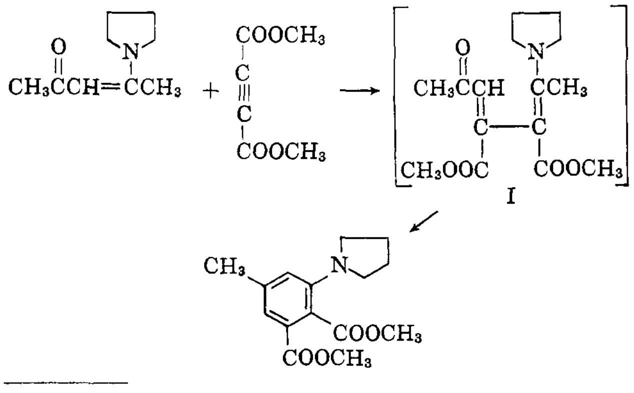
(6) J. A. Berson and E. M. Evleth, *Chem. Ind.* (London), 1362 (1961).

Communication TO THE EDITOR

A Method of Synthesis of the Benzene Ring

Sir:

The introduction by Stork and co-workers in 1954[1] of a new and useful method for the alkylation of carbonyl compounds awakened interest in the chemistry of enamines. A recent interesting new reaction of enamines was cited by Brannock.[2] He indicated that reaction with an acetylenecarboxylic acid ester interposes two carbon atoms between the α and β carbon of the enamine. This reaction, which we had been studying[3] independently, is capable of interesting and useful variations. One of these leads to a new synthesis of the benzene ring under mild conditions. The addition of dimethyl acetylenedicarboxylate to 4-pyrrolidino-3-penten-2-one dissolved in tetrahydrofuran results in a spontaneous reaction (presumably *via* I) with a temperature rise to 90°. The reaction mixture is diluted with water and the solid recrystallized from methanol to give dimethyl-4-methyl-6-pyrrolidinophthalate in 60% yield, m.p. 83–85°. [Calcd. for $C_{15}H_{19}NO_4$: C, 64.96; H, 6.91; N, 5.20. Found: C, 65.25; H, 6.92; N, 5.20. Ultraviolet spectrum in ethanol: λ_{max} 236 mμ (ϵ 16,400), 274 (7,950), and 347 (3,300).] Its structure is demonstrated by the presence of two isolated aromatic protons at 6.94 δ and 6.62 δ with indications of *meta* splitting and a three proton singlet at 2.27 δ due to an aromatic methyl group (A60, tetramethylsilane standard, deuteriochloroform solvent).



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CHARLES F. HUEBNER
ELLEN DONOGHUE

RECEIVED MARCH 1, 1963

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[1] G. Stork, A. Brizzolara, H. Landesman, J. Szmuskovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963), and preceding papers.

[2] K. C. Brannock, Abstracts of Papers, 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

[3] A paper with M. M. Robison and L. Dorfman is in preparation on the reaction of enamines (especially of cyclic ketones) with acetylenecarboxylic acid esters and other dienophiles.