EtOH), 250 mμ (ϵ 0.9 × 10^3), 257 (1 × 10^3), 261 (1 × 10^3), and 268 (0.9 × 10^3).

Anal. Calcd for $C_{19}H_{18}NBF_4$: C, 65.73; H, 5.23; N, 4.03. Found: C, 65.71; H, 5.45; N, 3.68.

Tri-*p*-anisylmethylammonium Tetrafluoroborate (2b).—To 0.7 g of tri-*p*-anisylamine[6] in 7 ml of dichloromethane was added 0.7 g of trimethyloxonium tetrafluoroborate.[5] The reaction vessel was degassed and sealed under vacuum. It was stirred at 75° for 7 days. The resulting blue solution was evaporated to dryness and the recovered material was successively washed with diethyl ether to give an ether-insoluble solid. Recrystallization from absolute ethanol gave 0.5 g of solid with mp 173.0–175.0°. An analytical sample had mp 175.5–176.0°; nmr ($CDCl_3$), δ 3.85 (s, 9, OCH_3), 4.54 (s, 3, $^+NCH_3$), 6.8–7.4 (m, AA'BB', 12, C_6H_4); ir, 3.3 (m), 6.3 (s), 6.7 (s), 6.9 (s), 7.0 (s), 7.7 (s), 7.9 (s), 8.5 (s), 9.5 μ (vs); uv max (absolute EtOH), 234 mμ (ϵ 2.9 × 10^4), 273 (5.1 × 10^3), 281 (4.3 × 10^3).

Anal. Calcd for $C_{22}H_{24}NO_3BF_4$: C, 60.43; H, 5.53; N, 3.20. Found: C, 60.47; H, 5.62; N, 3.28.

Base Reactions.—The lithium bases were obtained commercially (Foote or Alfa chemicals) as was the potassium *t*-butoxide (M. S. A. Research Corp., Callery, Pa.). The potassium methoxide was prepared by carefully adding potassium metal to ice-cold methanol. Solvents were dried and distilled.

A typical run is as follows. To the required amount of quaternary ammonium salt in a dry, nitrogen-purged vessel was placed the calculated amount of base and solvent was added. The materials were then allowed to react for the desired time. Water was added and the organic material was recovered by further extraction with ether or pentane.

The kinetic runs were carried out by adding the required amount of basic reagent to a solution of the salt in methanol-OD in an nmr tube at 0°. The tube was purged with nitrogen, then the progress of the reaction followed at 0° by observing the decrease in the aromatic resonance of the salt and the appearance of the aromatic resonance of the tertiary amine.

Registry No.—2a, 16457-64-0; 2b, 16457-65-1.

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Benzene-Induced Nuclear Magnetic Resonance and Dipole Moment Shifts of Five-Membered Rings Containing Heteroatoms

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Received January 25, 1968

The five-membered ring heterocycles provide an interesting series of compounds to investigate the factors which affect the benzene solvent shift in the nmr spectra because their geometry is fixed, there are only two basic types of protons (if the plane of the ring is a symmetry plane), and the chemical shifts of the α and β protons are generally well separated. Benzene solvent shifts of the high resolution nuclear magnetic resonance (nmr) spectra have been reported[1–5] as useful in elucidating the proton geometry in carbonyl compounds. Protons behind the carbonyl carbon are shielded while those in front are deshielded with respect to the corresponding values in CCl_4. Shielding effects have also been observed for other functional groups.[6–14] Some generalizations have been made[11] concerning the mechanism of the shielding effects on the solute molecules in benzene. The solvent shifts are thought to result from the formation of a nonplanar association between the solute molecule and benzene at a local electron-deficient site in the solute. The orientation of the benzene is believed[11] to be such that the benzene ring avoids the negative end of the dipole in a nonplanar preferred configuration. A benzene molecule appears to be associated with each electron deficient site in the solute molecule. It is convenient to depict the nonplanar average association between benzene and the heteroatom-containing solute as a "complex;" however, the use of the term "complex" in this context only implies the effects resulting from a slight minimum in the potential energy surface of the benzene–solute molecular interactions.

The following expression, analogous to that of Bhacca and Williams,[15] was used to analyze the data

$$\Delta = \gamma_{CCl_4}{}^{H} - \gamma_{C_6D_6}{}^{H} \qquad (1)$$

where $\gamma_{CCl_4}{}^{H}$ = the center of resonance for a particular kind of proton at infinite dilution in CCl_4 with respect to TMS in CCl_4 and $\gamma_{C_6D_6}{}^{H}$ = the corresponding center of resonance in C_6D_6. The γ values in eq 1 will approach the corresponding chemical shift values (δ) as the system approaches first-order behavior. When planar five-membered ring molecules exist with benzene in solution, there is a certain amount of ordering due to the average planarity of the rings. In order to study only the ordering due to the heteroatom, a Δ value is determined for cyclopentane. The Δ values for the five-membered rings containing heteroatoms are only significant if they exceed this Δ value of cyclopentane. If we assume that the average configuration of the five-membered ring is planar, we note that for all solutes the plane of the five-membered ring is a plane of symmentry of the molecule. These compounds, together with their Δ and γ values, are listed in Table I. Also given in this table are the available literature values for the dipole moments in benzene. It can be seen from the values given that, for most compounds listed, the γ values are indeed chemical shifts.

Figure 1 shows a plot of the solvent shift (Δ^{β}) of the protons β to the functional group *vs.* the dipole moment in benzene ($\mu_{C_6H_6}$) for the molecules. Except for the selenium compound, there seeems to be a linear relationship between $\mu_{C_6H_6}$ and Δ^{β}. A similar relationship between the solvent shift of the α protons (Δ^{α}) is not as apparent. A correlation of the Δ's with dipole moment is expected in the absence of steric effects.[6,9] In general, the larger the dipole moment, the greater the electron deficiency of certain sites in the molecule.

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[1] J. D. Connally and R. McCrindle, *Chem. Ind.* (London), 379 (1965).

[2] N. S. Bhacca and D. H. Williams, *Tetrahedron*, **21**, 2021 (1965).

[3] C. J. Timmons, *Chem. Commun.*, 576 (1965).

[4] Y. Fujise and S. Itô, *Chem. Pharm. Bull.* (Tokyo), **14**, 797 (1966).

[5] D. W. Boykin, A. B. Turner, and R. E. Lutz, *Tetrahedron Lett.*, 817 (1967).

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[8] J. E. Anderson, *Tetrahedron Lett.*, 4713 (1965).

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[12] M. Honda, Y. Kawasaki, and T. Tanaka, *Tetrahedron Lett.*, 3313 (1967).

[13] Y. Kawasaki, *Mol. Phys.*, **12**, 287 (1967).

[14] D. J. Barraclough, P. W. Hickmott, and O. Meth-Cohn, *Tetrahedron Lett.*, 4289 (1967).

[15] N. S. Bhacca and D. H. Williams, *ibid.*, 3127 (1964).

TABLE I

SOLVENT SHIFTS AND FREQUENCIES OF CENTERS OF RESONANCE FOR FIVE-MEMBERED RINGS[a]

Compound	$\gamma_{CCl_4}{}^{\alpha}$	$\gamma_{C_6D_6}{}^{\alpha}$	Δ^{α}	$\gamma_{CCl_4}{}^{\beta}$	$\gamma_{C_6D_6}{}^{\beta}$	Δ^{β}	$\mu_{C_6H_6}{}^{b}$
Cyclopentane	150.9	145.6	5.3	...	...	...	0
Tetrahydrofuran	362.1	357.7	4.4	179.6	142.1	37.5	1.69
Tetrahydrothiophene	275.5	254.2	21.3	191.8	146.5	45.3	1.89
Tetrahydroselenophene	340.5	274.1	66.4	204.0	140.2	63.8	1.81
Tetrahydrotellurophene	311.8	283.8	28.0	204.1	161.5	42.6	...
Cyclopentanone	205.4[c]	170.4[c]	35.0	192.2[c]	130.2[c]	62.0	2.93
Tetramethylenesulfone	291.0	227.2	63.8	218.7	119.0	99.7	4.69
Methylenecyclopentane[d]	222.8	217.9	4.9	165.2	148.0	17.2	...
Tetrahydrotellurophene dibromide	387.1	288.7	98.4	292.1	202.0	90.1	...

[a] All γ and Δ values are in units of cycles per second and the dipole moments (μ) are in Debye units. Measurements were made at 100 Mc. [b] Taken from A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963. [c] The α and β chemical shifts were very similar. The Δ values, therefore, were derived by following individual lines rather than centers of resonance. [d] The olefinic protons are deshielded by 18.2 cycles.

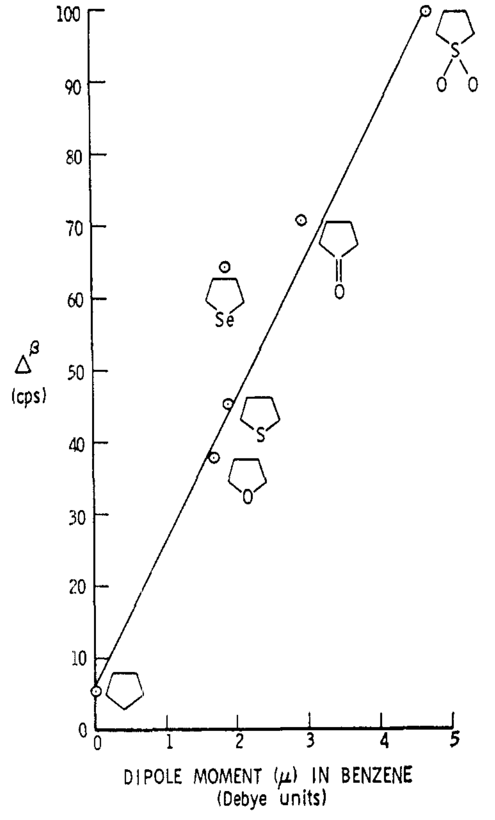

Figure 1.—Plot of dipole moments *vs.* solvent shifts of β protons.

As benzene is believed[11] to solvate electron-deficient sites preferentially, the molecule with the highest dipole moment should show the greatest solvent shift. Steric hindrance will modify this simple picture; and perhaps cause the anomaly in the β-proton shift of tetrahydroselenophene, as well as the nonlinearity of the α-proton shifts.

In order to test independently the validity of the postulated benzene–solute "complexes," the dipole moments of tetrahydrofuran, tetrahydrothiophene, and tetrahydroselenophene were measured in carbon tetrachloride. If an association of the type described above actually exists, the dipole moments of each of these solute molecules in carbon tetrachloride should be changed with respect to benzene. Intuitively, one might expect that the dipole moments should be greater in carbon tetrachloride, for the π electrons of benzene should act to neutralize the dipole. Our results in carbon tetrachloride, together with redeterminations of two results in benzene, are shown in Table II. In accordance with expectation, the dipole moments of tetrahydrofuran and tetrahydrothiophene are indeed greater in carbon tetrachloride. Tetrahydroselenophene is anomalous; however, steric effects of the heteroatom must be greatest in this case.

TABLE II

DIPOLE MOMENTS

Compound	$\mu_{CCl_4}{}^{25°}$	$\mu_{C_6H_6}{}^{a}$	$\mu_{C_6H_6}{}^{25° b}$
Tetrahydrofuran	1.82 ± 0.02	1.69	1.66 ± 0.02
Tetrahydrothiophene	1.98 ± 0.02	1.89	1.85 ± 0.02
Tetrahydroselenophene	1.64 ± 0.02	1.81	...

[a] At 20°, H. de v. Robles, *Rec. Trav. Chim.*, **58**, 111 (1939), taken from Table I, footnote *b*. [b] This work.

Experimental Section

Nmr Measurements.—A 5% solution was prepared for each solute in both carbon tetrachloride and deuteriobenzene. TMS was employed as an internal reference. All spectra were taken on a Varian HA 100 nmr spectrometer. Frequencies of all prominent lines were measured with a Hewlett-Packard 522-B electronic counter which has a precision of ±0.1 cps. The solutions were repeatedly diluted by 50% until there were no line shifts between successive dilutions.

Materials.—The following commercially available chemicals were measured without further purification: cyclopentane (Aldrich), tetrahydrofuran (J. T. Baker, boiling range 65.5–65.9°), tetrahydrothiophene (Eastman), cyclopentanone (Eastman), tetramethylene sulfone (Aldrich Chemical Co.), and methylene cyclopentane (K & K).

Tetrahydroselenophene was synthesized by the procedure of Morgan and Burstall.[16] The product was doubly distilled under nitrogen before use. Tetrahydrotellurophene dibromide was formed by the method of Farrar and Gullend,[17] mp 127.5–130.5° (lit.[17] mp 128–131°). Tetrhydrotellurophene was synthesized from the dibromide by the procedure of Morgan and Burstall[18] and was distilled under nitrogen just before use. The carbon tetrachloride (Eastman Technical grade) was also distilled before use and found to contain less than 0.1 mg/ml of impurities after distillation. Deuteriobenzene (99.7%) was obtained from Merck Sharp and Dohme. The purity of tetrahydrothiophene, used for dipole moment measurements, was checked by gas phase chromatography and the compound found to be free of impurities. The tetrahydrofuran was distilled from sodium just prior to being used. Thiophene-free benzene (Baker Analyzed) was distilled from sodium before use in dipole moment studies.

Dipole Moments.—Dielectric constants were measured for a series of carbon tetrachloride and benzene solutions of each compound. All measurements were made in an oil bath at 25° and at a frequency of 1 MHz by means of a Wayne–Kerr transformer ratio arm bridge, Model B601. The capacity of the dielectric cell was measured by a substitution method, using a General Radio Type 1422D variable capacitor. The cell is of a type

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(16) G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1096 (1929).

(17) W. V. Farrar and J. M. Gullend, *ibid.*, 11 (1945).

(18) G. T. Morgan and F. H. Burstall, *ibid.*, 180 (1931).

TABLE III

Compound	ϵ_1	V_1, ml/g	α	β, ml/g	P_2, cc	MR$_D$, cc	μ, D
Tetrahydrofuran[a,b]	2.2280	0.63085	8.59	0.4667	88.59	20.08	1.82
Tetrahydrothiophene[b]	2.2267	0.63078	8.90	0.3344	107.80	26.41	1.98
Tetrahydroselenophene[b]	2.2268	0.63085	3.98	0.1069	85.86	29.19	1.64
Tetrahydrofuran[c]	2.2725	1.14445	4.02	−0.0243	77.62	20.08	1.66
Tetrahydrothiophene[c]	2.2725	1.14445	4.34	−0.1542	97.94	26.41	1.85

[a] ϵ = dielectric constant, V_1 = specific volume, $\alpha = (\epsilon_{12} - \epsilon_1)/W_2$, $\beta = (V_{12} - V_1)/W_2$, W = weight fraction, P = polarization, MR$_D$ = molar refraction. Subscripts: 1, solvent; 2, solute; 12, solution. [b] Measurements carried out in carbon tetrachloride. [c] Measurements carried out in benzene.

designed by Sayce and Briscoe;[19] the air capacitance is 25.99 pF. The cell constant, C_0, was determined from the capacitance, C_a, of the cell containing dry air and the capacitance, C_x, of the cell containing a liquid of known dielectric constant, ϵ, such as benzene or carbon tetrachloride.[20] The cell constant is given by $C_0 = (C_a\epsilon - C_x)/(\epsilon - 1)$.

Solution densities were measured at 25° with a pycnometer that had been calibrated with pure benzene, bp 79.6° (746 mm) (lit.[21] bp 79.6° (746 mm)).

The method of Halverstadt and Kumler[22] was used to calculate the dipole moments. The advantages of this method of treating solution data have been evaluated by Smyth.[23] The electronic polarization is taken as equal to the molar refraction of the solute. The atomic polarization may be assumed, with negligible error,[23] equal to 5% of the electronic polarization. The molar refractions are calculated from electron group refractions.[24] The dipole moments are calculated as

$$\mu = 0.22125({}_\infty P_2 - 1.05\text{MR}_\text{D})^{1/2}$$

In this case, dielectric constants and specific volumes of the carbon tetrachloride and benzene solutions are found to be linear functions of the solute weight fraction over the range studied. The experimental and calculated quantities used to compute the dipole moment are given in Table III.

Registry No.—Benzene, 71-43-2; cyclopentane, 287-92-3; tetrahydrofuran, 109-99-9; tetrahydrothiophene, 110-01-0; tetrahydroselenophene, 3465-98-3; tetrahydrotellurophene, 3465-99-4; cyclopentanone, 120-92-3; tetramethylenesulfone, 126-33-0; methylenecyclopentane, 1528-30-9.

Acknowledgments.—The authors wish to thank L. E. Nelson for making the nmr measurements and Mobil Research and Development Corp. for permission to publish this work.

[19] L. A. Sayce and H. V. A. Briscoe, *J. Chem. Soc.*, 315 (1925).

[20] R. J. W. LeFevre, "Dipole Moments," Methuen and Co., Ltd., London, 1953, p 53.

[21] "Handbook of Chemistry and Physics," K. C. Weast, Ed., The Chemical Rubber Publishing Co., Cleveland, 1964, p D-124.

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

[23] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N.Y. 1955, p 224.

[24] See ref 23, p 409.

Acid-Catalyzed Ring Opening of 6,8-Dinitro-1,3-benzodioxane

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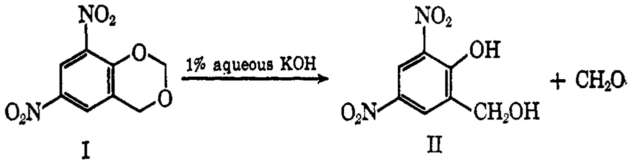
Received December 11, 1967

The preparation of 6,8-dinitro-1,3-benzodioxane (I) by the nitration of 6-nitro-1,3-benzodioxane was first described by Chattaway and Irving.[1] Their subsequent investigation[2] revealed that the 6,8-dinitro-1,3-benzodioxane was easily cleaved by dilute alkali to give 2-hydroxy-3,5-dinitrobenzyl alcohol (II).



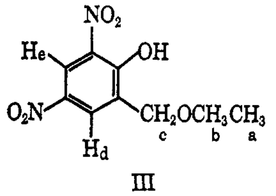
I II

In contrast to this, 6-nitro-1,3-benzodioxane was stable to boiling 25% aqueous alkali or alcoholic potassium ethoxide. Chattaway and Irving then postulated that the stability of this dioxane system toward alkali was decreased by electron-withdrawing groups in the 8 position.

The present investigation has led to the discovery of an acid-catalyzed ring cleavage of 6,8-dinitro-1,3-benzodioxane.

Results and Discussion

The yield of expected product from the nitration of 6-nitro-1,3-benzodioxane was dependent upon the reaction conditions employed. After 20 min at 0° the nitration gave good yields. Prolonged acid treatment at 40–50° led to oxidation and formation of dinitrosalicylic acid as well as the expected product. At intermediate temperatures (10–20°) small quantities of another by-product were formed. This acidic compound (NE 240 ± 2) was precipitated by the addition of water to the ethanolic mother liquor of recrystallization of crude 6,8-dinitro-1,3-benzodioxane and was shown to be 2,4-dinitro-6-ethoxymethylphenol (III) by synthesis using a previously described[3] procedure.



III

Nmr, δ
a, 1.33 (t)
b, 3.71 (q)
c, 4.66 (t, J = 0.7 Hz)
d, 8.62 (d, J = 3.0 Hz)
e, 8.97 (d, J = 3.0 Hz)

The ethoxy compound III and the corresponding methyl ether were found to arise from the dioxane I on treatment with the respective alcohols containing nitric acid. To avoid complications caused by the oxidative properties of nitric acid, the reaction was then performed using an aprotic Lewis acid. A butanol solution of 6,8-dinitro-1,3-benzodioxane containing 1 ml of boron

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[1] F. D. Chattaway and H. Irving, *J. Chem. Soc.*, **1931**, 2492.

[2] F. D. Chattaway and H. Irving, *ibid.*, **1934**, 325.

[3] (a) Indian Patent 91,371 (June 1965); (b) French Patent 1,403,658 (Oct 1965).