

Fig. 4.—Analyzed ν_{\max} values for the lowest charge-transfer band of various substituted benzenes with TCNE plotted against ionization potential of the donor: I, "theoretical" curve $h\nu_{CT} = I_D - 6.10 + 0.54/(I_D - 6.10)$; II, best experimental line $h\nu_{CT} = 0.83I_D - 4.42$ showing vertical error limits; III, Kuroda's line drawn through the points for benzene (1) and naphthalene (9); 2, chlorobenzene; 3, *p*-dichlorobenzene; 4, *o*-dichlorobenzene; 5, bromobenzene; 6, *p*-chlorotoluene; 7, 1,3,5-trimethylbenzene; 8, 1,2,3-trimethylbenzene; 10, anisole.

(4) Overlapped charge-transfer bands must be decomposed as in the present work.

(5) As a result of meeting the above conditions (and any other relevant ones), the change in donor ionization potentials must be the predominant variable as the donor changes. This condition is fairly well met, for example, in the case of the polycyclic aromatics, but less so for many substituted benzenes, where there may be substantial changes in charge distribution with little variation in ionization potential.

TABLE II

IONIZATION POTENTIALS OF SOME SUBSTITUTED BENZENES FROM THEIR CHARGE-TRANSFER ENERGIES WITH TCNE^a

Substituted benzene donor	$h\nu_{CT}$, e.v.	I_D , e.v. ^b
1-Bromo-2-methoxy-	2.45	8.3
1-Bromo-4-methoxy-	2.39	8.2
1-Chloro-2-methoxy-	2.49	8.3
1-Chloro-4-methoxy-	2.43	8.25
1,4-Dibromo-	2.95	8.9
1,2-Dimethoxy-	2.09	7.8
1,3-Dimethoxy-	2.22	8.0
1,4-Dimethoxy-	1.96	7.7
1-Methyl-2-methoxy-	2.27	8.1
1-Methyl-3-methoxy-	2.33	8.1
1-Methyl-4-methoxy-	2.22	8.0
Thiomethoxy-	2.17	7.9
1,3,5-Trichloro-	3.47	9.5
1,2,4-Trimethoxy-	1.81	7.5
1,2,3-Trimethoxy ^c	2.41	8.2

^a Calculated from eq. 8. ^b ± 0.15 . ^c Unexpectedly high charge-transfer energy, probably due to steric effects in the donor.

In Table II we give a few examples of ionization potentials derived in this way from eq. 9. Because this is an average line relating many different TCNE complexes, the error is inevitably high. The results may be useful, however, for molecules too volatile for direct ionization potential measurement. We believe that accuracy may be improved by obtaining the reference line from a group of donors closely related to the one under investigation, and propose to test this matter further. At present, however, our line for the methylated, halogenated, and methoxybenzenes, while they appear to show some differences, are very nearly within the limits of experimental error. They have, therefore, not been included or used in this paper.

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Electron Donor Ability of 7-Oxabicyclo[2.2.1]heptane

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The thermodynamic constants for the complexation of 7-oxabicyclo[2.2.1]heptane with iodine in *n*-heptane were determined by a study of the temperature dependence of the perturbed iodine absorption in the visible region and the charge-transfer (CT) band in the ultraviolet region. The hydrogen-bonding interactions of this ether with methanol-*d* and with phenol were measured by the respective O-D and O-H shifts. Nuclear magnetic resonance data for the δ -shift and for the $J_{C^{13}-H}$ coupling constant of the α -protons were determined. Comparable data were taken for the four-, five-, and six-membered ring saturated cyclic ethers. The composite data indicate an electron donor ability of 7-oxabicyclo[2.2.1]heptane which is less than that of oxetane, but somewhat greater than that of tetrahydrofuran and tetrahydropyran. This relative order differs from that found from pK_a measurements in aqueous acid, which show the bridged ether to be the weakest base. This difference is attributed to a solvation effect.

Introduction

Studies on hydrogen bonding¹ and on iodine complexation^{2,3} with saturated cyclic ethers showed their basicity order to be four- > five- > six- > three-mem-

bered ring.¹ These results have been attributed to a change in electron distribution around the atoms in the ring with change in ring size.

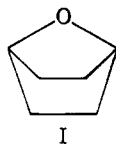
Recently, Arnett and Wu^{4,5} have measured directly the pK_a 's of a number of saturated ethers in sulfuric

(1) S. Searles and M. Tamres, *J. Am. Chem. Soc.*, **73**, 3704 (1951).
 (2) M. Brandon, M. Tamres, and S. Searles, *ibid.*, **82**, 2129 (1960).
 (3) M. Tamres and M. Brandon, *ibid.*, **82**, 2134 (1960).

(4) E. M. Arnett and C. Y. Wu, *ibid.*, **84**, 1680 (1962).
 (5) E. M. Arnett and C. Y. Wu, *ibid.*, **84**, 1684 (1962).

acid. In the case of the cyclic ethers, good linear correlation was found with the results obtained toward other acids.⁵ Unfortunately, the three- and four-membered rings could not be studied because of their sensitivity to aqueous acid, analogous to the situation which has been found with boron trifluoride.⁶

However, Arnett and Wu⁵ did study 7-oxabicyclo[2.2.1]heptane (I). The strain in this molecule results



in a COC bond angle which should approach that in trimethylene oxide and, because of the ring size sequence, should exhibit a high basicity. The fact that the pK_a was found to be smaller than that of tetrahydrofuran led to an explanation in terms of electron correlation. Presumably in tetrahydrofuran (and oxetane) repulsion between the lone-pair electrons on the oxygen and the bonding electrons of the nearby C-H groups serves as a driving force for proton addition and, hence, increases the basicity. In tetrahydropyran and in 7-oxabicyclo[2.2.1]heptane, the low basicities are explained by a decrease in the nonbonded repulsive force due to the staggered conformation of the lone-pair electrons and the adjacent C-H bonds.

There is, however, another factor which should be considered in studies in aqueous acid, namely, the role of solvation. In the case of 7-oxabicyclo[2.2.1]heptane, the oxygen is partially surrounded by a "hydrocarbon cage" which reduces the chance of solvent stabilization of the ion formed on proton addition. It is well established that solvation of the ionic species is an important factor in determining acidity, and this situation would surely be predicted to diminish the pK_a relative to a less hindered analog. Therefore, it was thought worthwhile to study this bridged ether by methods where solvent effects would be minimized.

Experimental

Apparatus and Procedure.—The spectrophotometric apparatus and techniques used to study iodine complexation have been described previously.^{2,3,7} The measurement of O-D shifts in methanol-*d*¹ and of O-H shifts in phenol⁸ also have been sufficiently described.

N.m.r. spectra were taken on a Varian A-60 instrument.

Materials.—The source of iodine, of *n*-heptane, and of the simple cyclic ethers (oxetane, tetrahydrofuran, and tetrahydropyran) has been given.²

7-Oxabicyclo[2.2.1]heptane was prepared by a previously described method⁹ involving the cyclization of 50 g. of *cis*- and *trans*-1,4-cyclohexanediol by heating with 60 g. of freshly roasted alumina at 240–275°. Fractional distillation of the product gave 3 g. of pure 7-oxabicyclo[2.2.1]heptane, b.p. 118° (uncor.), n_{20}^D 1.4496 (lit. b.p. 117–118°,⁹ 120.1°,¹⁰ n_{20}^D 1.4477¹⁰), plus other fractions that were less pure. Gas chromatographic analysis indicated that the product was at least 99.5% pure. Additional material was obtained from Prof. Arnett.

Calculations.—Absorption data for the 7-oxabicyclo[2.2.1]heptane-iodine complex were taken in both the visible and ultraviolet regions using a solution of *n*-heptane-iodine as the blank. The spectrophotometric equation which applies to this experimental condition is⁷

$$\frac{C_B b C_Z}{A} = \frac{C_B + C_Z}{(a_c - a_z)} + \frac{1}{K_c(a_c - a_z)} - \frac{A}{b(a_c - a_z)^2}$$

where C_B = donor concentration, C_Z = acceptor concentration, b = cell length, A = absorbance, a_c = molar absorptivity index of the complex, a_z = molar absorptivity index of the free acceptor, and K_c = association constant (in l. mole⁻¹). Dropping of the last term, to reduce the above equation from a quadratic to a linear form, made no difference whatsoever on the values of K_c and a_c . This is to be expected when complexes are not very strong.¹¹ All calculations were programmed for the IBM 7090 computer. The error limits for K_c were determined using the method of Fieller.¹²

Results

Data for the association constants and molar absorptivity indices for the 7-oxabicyclo[2.2.1]heptane-iodine complex for both the blue shift in the visible region and the charge-transfer (CT) band in the ultraviolet region are given in Table I. The molar absorptivity indices in the visible region are fairly constant with temperature, except that at 6.7°. The variation in the ultraviolet region is much greater. Since any error in the molar absorptivity index results in a corresponding error in the calculation of the equilibrium constant, average values of $a_c - a_z$ were employed to calculate K_c at each temperature, and these were used in the plot of $\log K_c$ vs. $1/T$ shown in Fig. 1. The ther-

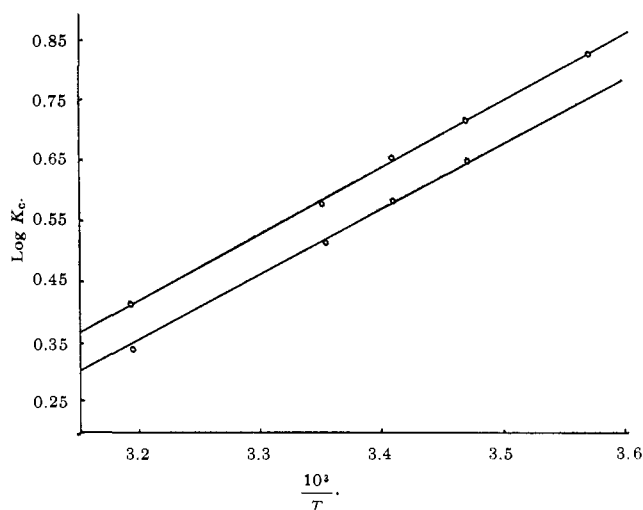


Fig. 1.— $\log k_c$ vs. $1/T$ for 7-oxabicyclo[2.2.1]heptane-iodine complex: upper line, ultraviolet region; lower line, visible region. K_c was calculated from the product $K_c(a_c - a_z)$ using the average value for $a_c - a_z$ obtained over the temperature range.

modynamic results are tabulated in Table II¹³ and may be compared with previously obtained data on cyclic ethers.

Also given in Table II are hydrogen-bonding data for 7-oxabicyclo[2.2.1]heptane and for the four-, five-, and six-membered ring saturated cyclic ethers with methanol-*d* and with phenol. The methanol-*d* results for the simple cyclic ethers are in the same sequence, but slightly different from those reported previously.^{1,14} The observed O-H band of phenol in CCl_4 at 3612

(11) M. Tamres, *J. Phys. Chem.*, **65**, 654 (1961).

(12) E. C. Fieller, *J. Roy. Statist. Soc., Appendix Suppl.*, **7**, 1 (1940).

(13) Even by averaging $a_c - a_z$, the point at 6.7° in the visible region in Fig. 1 seems somewhat displaced relative to the other four points. If this point is omitted from the calculation, the resulting thermodynamic values are: $\Delta H^\circ = -5.07 \pm 0.05$ kcal./mole, $\Delta F^\circ_{298} = -0.720$ kcal./mole, and $\Delta S^\circ = -14.6 \pm 0.2$ e.u.

(14) A CaF_2 prism was used in the present study; LiF was used previously.

(6) D. E. McLaughlin, M. Tamres, and S. Searles, *J. Am. Chem. Soc.*, **82**, 5621 (1960).

(7) M. Tamres and S. Searles, *J. Phys. Chem.*, **66**, 1099 (1962).

(8) P. von R. Schleyer and R. West, *J. Am. Chem. Soc.*, **81**, 3164 (1959).

(9) E. A. Fehnel, S. Goodyear, and J. Berkowitz, *ibid.*, **73**, 4978 (1951).

(10) R. C. Oldberg, H. Pines, and V. N. Ipatieff, *ibid.*, **66**, 1096 (1944).

TABLE I
7-OXABICYCLO[2.2.1]HEPTANE-IODINE COMPLEX IN
n-HEPTANE

Temp., °C.	K_c , ^a l. mole ⁻¹	$a_c - a_z$,
		l. mole ⁻¹ cm. ⁻¹
Visible region		
6.7	5.06 ± 0.15	930 ^b
14.9	4.51 ± .06	868
19.8	3.95 ± .04	855
25.0	3.32 ± .04	869
40.0	2.25 ± .03	856
Ultraviolet region		
6.7	6.24 ± 0.06	9590 ^c
14.9	5.07 ± .08	9170
20.1	4.55 ± .12	8850
25.2	3.74 ± .12	9120
40.1	2.99 ± .16	7790

^a For 50% confidence interval. ^b Values in the visible region for λ_{\max} 455 m μ . ^c Values in the ultraviolet region for λ_{\max} 244 m μ .

TABLE II
COMPARISON OF 7-OXABICYCLO[2.2.1]HEPTANE WITH OTHER CYCLIC ETHERS

Ether	I ₂ complex ^a			Methanol- <i>d</i> ^b O-D shift, cm. ⁻¹	Phenol ^c O-H shift, cm. ⁻¹	δ -Values α -protons	$J_{C^{12}-H}$ α -protons, c.p.s.	$-pK_a$ ^d
	$-\Delta H^\circ$, kcal./mole	$-\Delta F^\circ_{298}$, kcal./mole	$-\Delta S^\circ$, e.u.					
7-Oxabicyclo[2.2.1]heptane								
Visible	4.74 ± 0.21 ^e	0.706	13.5 ± 0.7 ^e	114	320	4.50	157 ^f	2.80
Ultraviolet	4.94 ± .07 ^e	.806	13.8 ± .2 ^e					
Oxetane	6.4 ± .2 ^g	.79 ^g	18.8 ± .8 ^g	121	339	4.71	150	
Tetrahydrofuran ^h	5.3 ± .2 ^g	.56 ^g	15.4 ± .8 ^g	113	314	3.67	148	2.08
Tetrahydropyran	4.9 ± .2 ^g	.52 ^g	14.5 ± .8 ^g	110	305	3.60	143	2.79

^a In *n*-heptane. ^b Relative to O-D band of methanol-*d* in CCl₄ found at 2690 cm.⁻¹; CaF₂ optics and 0.1-mm. NaCl cell. Precision is good to about ±1 cm.⁻¹. ^c Relative to O-H band of phenol in CCl₄ found at 3612 cm.⁻¹; CaF₂ optics and 0.1-mm. NaCl cell. Precision is good to about ±3 cm.⁻¹. ^d Reference 5. ^e Standard deviation. ^f Diffuse band, difficult to pick out the center. ^g Ref. 2, combined visible and ultraviolet data. The ΔF° and ΔS° data in ref. 2 have been altered by ±1.14 kcal./mole and -3.8 e.u., respectively, as a consequence of changing the equilibrium constant units from K_x to K_c (see ref. 3, footnote 12).

cm.⁻¹ compares favorably with that at 3610 cm.⁻¹ reported by Schleyer and West.⁸

Nuclear magnetic resonance studies of the δ -shifts and $J_{C^{12}-H}$ coupling constants of the α -protons also were made for this set of cyclic ethers, and the results are listed in Table II.¹⁵

Discussion

The composite free energy data for the iodine complexation with 7-oxabicyclo[2.2.1]heptane, obtained from the study of the perturbed iodine band in the visible region and the CT band in the ultraviolet region, when compared with similar data for the other cyclic ethers indicate that the sequence of electron donor ability is oxetane > 7-oxabicyclo[2.2.1]heptane > tetrahydrofuran > tetrahydropyran. Since for a series of related donors there generally is a correlation among the free energy, the enthalpy, and the entropy of complex formation with a given acceptor,^{3,16,17} in the absence of steric factors, the enthalpy results for the bridged ether with iodine seem somewhat low. However, except for oxetane, the spread in the enthalpy data is within a rather narrow range.

(15) A very precise set of n.m.r. data for δ -shifts and $J_{C^{12}-H}$ coupling constants recently has been reported by E. Lippert and H. Prigge, *Ber. Bunsenges. physik. Chem.*, **67**, 415 (1963).

(16) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **77**, 2164 (1955)

(17) P. A. D. de Maine, *J. Chem. Phys.*, **26**, 1199 (1957).

Support for the above donor sequence is found in the hydrogen-bonding studies with both methanol-*d* and phenol.

It had been noted that, at least for the cyclic ethers,¹⁸ the low electron shielding of the α -protons correlated with the high electron donor ability of the oxygen. It is interesting to note that the n.m.r. data for 7-oxabicyclo[2.2.1]heptane show a δ -value intermediate between that of oxetane and tetrahydrofuran.

It has recently been pointed out that $J_{C^{12}-H}$ coupling constants could be correlated with the ring angle in cycloalkanes.¹⁹ The coupling constants also vary with ring size in the saturated heterocyclics.¹⁵ Comparison with the bicyclic ether can be made only in a qualitative way because of the inductive effect due to replacing one of the α -hydrogens in the bridged structure. If a reasonable allowance of about 5 c.p.s. is made, the coupling constant data are suggestive of a structural similarity between the bicyclic ether and oxetane.

There is no question that the pK_a data obtained in aqueous sulfuric acid show 7-oxabicyclo[2.2.1]heptane to be a weaker electron donor than either tetrahydrofuran or tetrahydropyran.⁵ On the other hand, the bulk of the evidence in nonaqueous studies indicates that the inverse order holds. The postulate that repulsion between the lone-pair electrons on the oxygen atom and the bonding electrons of the α -C-H bond might contribute to the driving force in enhancing electron donor properties of the molecule cannot be completely ruled out. However, it cannot be the dominant factor in the present case because of the reversal in basicity order observed when changing from aqueous medium. It seems more likely that the low basicity of the bridged ether in aqueous sulfuric acid is due primarily to a diminished solvation energy in stabilizing the protonated ether as a consequence of the "hydrocarbon cage" which shields one side of the oxygen atom.

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(18) This correlation does not appear to hold for the cyclic sulfides (ref. 7).

(19) C. S. Foote, *Tetrahedron Letters*, 579 (1963).