methoxycyclohexanol (VII), b.p. 90–95° (10 mm.) n_D^{25} 1.4650.

The distillation residue afforded 2 g. of recovered *trans*-1,4-cyclohexanediol on crystallization from acetone, m.p. 141–142°.

The *p*-toluene sulfonate and 3,5-dinitrobenzoate of VII were prepared, m.p. 65–66° and 126–127°, respectively.

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Conformational Analysis. VII. The Dipole Moment of 2-Bromocyclooctanone[1,2]

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Recently a conformational analysis of the 2-bromocyclooctanone molecule (I) was reported.[3] This molecule was predicted to exist as a mixture of the five conformational species III–VI[4] depicted in Fig. 1. (There are two species having the gross geometry of III which differ in dihedral angle.) The percentage compositions of the equilibrium mixtures of III–VI (see Table I) in the solvents *n*-heptane benzene, and dioxane were calculated from theoretical considerations and these values predicted rather small changes in the position of the conformational equilibrium with respect to the effective dielectric constant of the medium. A small influence of solvent upon the equilibrium composition was detected by experimental measurements of the absorption intensities of the infrared and ultraviolet carbonyl absorption maxima of I in various media and these spectral data were qualitatively consistent with the theoretical predictions. The exact extent of the agreement between theory and experiment was somewhat obscured, however, by the fact that at present there is no theory available which could be used to quantitatively predict the results of the spectral measurements. On the other hand, the determination of the dipole moment of I in benzene solution did provide an accurate physical measurement which could be directly compared to a calculated value. The experimental value of 3.36 D was in excellent agreement with the predicted dipole moment of 3.28 D for the compound in this solvent.

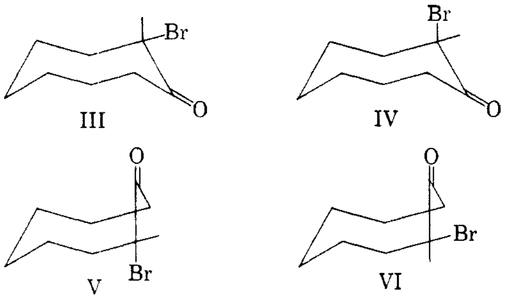

Figure 1

TABLE I

CALCULATED PERCENTAGE CONFORMATIONAL ISOMER COMPOSITION OF 2-BROMOCYCLOOCTANONE

Conformational Isomer	Dihedral Angle	Solvent (D_{effec}) *n*-Heptane (4.83)	Benzene (6.44)	Dioxane (10.3)
IIIa	40°	16	19	22
IIIb	63°	26	27	28
IV	166°	2	1	1
V	132°	47	41	34
VI	12°	9	12	15

The present study was undertaken to extend the dipole moment data for 2-bromocyclooctanone to the solvents *n*-heptane and dioxane and thus to provide a more extensive experimental test of the theoretical analysis. The dipole moments of I were obtained from dielectric constant measurements and had the values 3.29 D and 3.42 D in the solvents *n*-heptane and dioxane, respectively. These values, along with the experimental dipole moment of I in benzene solution and the dipole moments calculated from the estimated compositions for each solvent of Table I, are listed in Table II.

TABLE II

DIPOLE MOMENT OF 2-BROMOCYCLOOCTANONE AT 25°

Solvent	μ Calcd.	μ Observed
n-Heptane	3.13	3.29
Benzene	3.28	3.36
Dioxane	3.41	3.42

The qualitative prediction that only small changes in the conformational composition of the equilibrium mixture of IIIa–VI would result from the changing effective dielectric constant is substantiated by the small differences observed between the magnitudes of the dipole moment in each solvent. The deviations between the calculated and observed moments as the solvent is varied appear to be systematic, but are certainly as small as could be hoped for. The variation of the dipole moment of 2-bromocyclooctanone with solvent is to be compared with the similar corresponding changes in the moment of 2-bromocyclohexanone.[5]

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(1) Sponsored by the Office of Ordnance Research, U. S. Army.

(2) Paper VI, *J. Org. Chem.*, **25**, in press (1959).

(3) J. Allinger and N. L. Allinger, *J. Am. Chem. Soc.*, **81**, 5736 (1959).

(4) For reference, the numbers assigned to these isomers in Paper V (ref. 3) have been retained herein.

(5) The dipole moments of 2-bromocyclohexanone in *n*-heptane, benzene, and dioxane, respectively, are 3.37, 3.50, and 3.64 D. [W. D. Kumler and A. C. Huitric, *J. Am. Chem. Soc.*, **78**, 3369 (1956)].

EXPERIMENTAL

The *n*-heptane solvent was freed from olefinic contaminant by passage through a silica gel chromatographic column and then dried by distillation from sodium metal. The dioxane solvent was purified according to the method of Fieser.[6]

Dipole moment study. The dipole moment of 2-bromocyclooctanone in *n*-heptane and dioxane solution was determined at 25°. The data were treated by the method of Halverstadt and Kumler,[7] and the actual calculations were performed by applying automatic computing methods with an IBM 650 computer as described earlier.[8]

The molar refractivity was calculated from standard values of atomic refractivities[9] and had the value 44.720 cc. Atomic polarization was neglected. The data are summarized in Table III.

TABLE III

DIPOLE MOMENT DATA FOR 2-BROMOCYCLOOCTANONE AT 25°

Dioxane Solvent

N_2	d_{12}	ϵ_{12}
0.0071283	1.031228	2.3191
0.0041682	1.029428	2.2697
0.0027629	1.028583	2.2465
0.0016669	1.027949	2.2283
0.0008651	1.027463	2.2143
0.0000000	1.026897	2.2013
$\alpha = 16.5874$ $\beta = 0.6039$ $\epsilon_1 = 2.2007$		
$d_1 = 1.026921$ $P_{2\infty} = 284.60$ $\mu = 3.426$D		
n-Heptane Solvent		
0.0079180	0.683125	1.9706
0.0059871	0.681701	1.9547
0.0041774	0.680434	1.9409
0.0024350	0.679182	1.9261
0.0012521	0.678316	1.9174
0.0000000	0.677423	1.9069
$\alpha = 8.0093$ $\beta = 0.7188$ $\epsilon_1 = 1.9070$		
$d_1 = 0.677422$ $P_{2\infty} = 266.67$ $\mu = 3.295$D		

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N-Bromocaprolactam

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In the course of investigating the halogenation of caprolactam we had occasion to prepare the heretofore unknown *N*-bromocaprolactam. We have found that *N*-bromocaprolactam is useful as a brominating agent in much the same manner as *N*-bromosuccinimide,[1] *N*-bromophthalimide[2] and *N*-bromo-5,5-dimethylhydantoin.[3] We have also found that the new *N*-bromo derivative functions in many instances as an oxidizing agent in the same manner as *N*-bromoacetamide.[4] Whereas the known *N*-bromo-derivatives usually require a peroxide catalyst and/or actinic light to initiate bromination, *N*-bromocaprolactam can be employed without the aid of a catalyst.

The *N*-bromocaprolactam can be prepared following the procedure of Oliveto[5] for the synthesis of *N*-bromoacetamide. However, the product obtained by this method is usually difficult to crystallize, and in most cases can be purified only after several recrystallizations from water. We have found that a relatively pure *N*-bromocaprolactam can be obtained by a modified procedure, which involves adding liquid bromine to an aqueous solution of caprolactam followed by the addition of 50% aqueous potassium or sodium hydroxide until the bromine color is discharged, and treating the resultant solution with common salt to precipitate the *N*-bromocaprolactam, which after several ice water washes, melts at 64–66°.

EXPERIMENTAL

N-Bromocaprolactam. Into a flask equipped with an agitator, thermometer, and dropping funnel was placed a mixture of 271.2 g. (2.4 mol.) of caprolactam and 90 ml. of water. The reaction mixture was cooled to about 0° by an ice-salt bath, following which 320 g. (2.0 mol.) of liquid bromine was added dropwise over a 30-min. period. After the addition was complete, 270 ml. of a 50% aqueous potassium hydroxide solution (previously cooled to 10°) was added dropwise maintaining the temperature of the reaction mixture below 10° throughout the addition. The resultant yellow solution was stirred at ice temperatures for an additional 2 hr., following which 80 g. of sodium chloride was added, effecting precipitation of the *N*-bromocaprolactam. The product was filtered, washed thoroughly with ice water, and dried at room temperature *in vacuo*. There was obtained 288 g. (75%) of *N*-bromocaprolactam; m.p. 64–66°.

Anal. Calcd. for $C_6H_{10}NOBr$: Br, 41.6; N, 7.3. Found: Br, 41.2; N, 7.0.

4-Bromoacetanilide. Into a flask equipped with an agitator and reflux condenser was placed a solution of 13.5 g. (0.1 mol.) of acetanilide in 100 ml. of chloroform. Then while stirring, 19.2 g. (0.1 mol.) of *N*-bromocaprolactam was added all at once. After a short induction period (*ca.* 15 min.), the reaction mixture began to reflux, after which the solution was stirred at room temperature for 2 hr. The solid residue obtained after evaporating the solvent was washed with cold water to remove the caprolactam formed during

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