

and the sharp peak (at  $3625\text{ cm.}^{-1}$ ) of the free hydroxyl group appeared. No study of the  $3400\text{ cm.}^{-1}$  region is reported; the work of Daasch and Hanninen and the present study appear to be complementary to each other, as far as (XVII) is concerned.<sup>20</sup>

### Experimental

The absorption measurements were carried out with a Perkin-Elmer model 12C infrared spectrometer, using a

(20) A more quantitative discussion of the applicability of structures (C) and (D) is given by E. Bergmann and co-workers, ref. (14).

sodium chloride prism. The experimental conditions are summarized in the Tables. Molecular weight determinations were carried out in benzene (about 1% solution) by the cryoscopic method.

Preparations and properties of compounds (XIV)–(XVIII) have been described previously.<sup>14</sup> (I), (II) and (VIII) were commercial products, which were purified by careful fractionation (column of approximately 15 plates). Compound (III) was prepared from ethylene oxide and methylamine according to Knorr and Matthes.<sup>21</sup>

**2-Methylamino-3-methyl-3-butanol (IX).**—A solution of 15 g. of 4,4,5-trimethyloxazolidine<sup>14</sup> in 60 cc. of methylcyclohexane was hydrogenated in presence of 3 g. of Raney nickel, at  $100^\circ$  and 1300–1500 p.s.i. After removal of the solvent, the product was fractionated in a Todd column; b.p.  $155^\circ$  (760 mm.), yield 10.5 g. (70%),  $n_D^{20}$  1.436 (literature<sup>22</sup> b.p.  $152\text{--}155^\circ$  (750 mm.),  $n_D^{20}$  1.4394).

Compounds (IV), (V) and (VI) were prepared by catalytic hydrogenation of the corresponding Schiff bases or oxazolidines at atmospheric pressure in the presence of palladium-charcoal (10%)<sup>23</sup> and compounds (VII), (X), (XI), (XII) and (XIII) by reduction of the corresponding oxazolidines with lithium aluminum hydride.<sup>24</sup>

(21) L. Knorr and H. Matthes, *Ber.*, **31**, 1069 (1898).

(22) C. M. Suter and A. W. Ruddy, *THIS JOURNAL*, **65**, 762 (1943).

(23) E. Gil-av, *ibid.*, **74**, 1346 (1952).

(24) E. D. Bergmann, D. Lavie and S. Pinchas, *ibid.*, **73**, 5662 (1951). In this paper, the substances listed as No. 1 in Table I and II are the 4-methylpentamethylene compound and 2-(*p*-methylcyclohexylamino)-3-methyl-3-butanol, respectively.

REHOVOTH AND TEL-AVIV, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, AND UNIVERSITY OF ILLINOIS]

## Hydrogen-bonding of Esters and Lactones. Site of Bonding and Effect of Ring Size

BY SCOTT SEARLES,<sup>1a</sup> MILTON TAMRES AND GORDON M. BARROW

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The effect of ring size on the electron donor ability of lactones is such that  $\delta$ -valerolactone is a better donor than  $\gamma$ -butyrolactone, which in turn is more effective than  $\beta$ -propiolactone. This order is the reverse, with respect to ring size, of that found with cyclic ethers. The difference appears to be due to the fact that the carbonyl oxygen is the principal site of hydrogen bonding rather than the alkoxy oxygen and that the resonance in the carbalkoxy group is dampened in the smaller ring structures. Evidence is presented which indicates this effect of ring size on the resonance in lactones and shows that the carbonyl oxygen is the primary site of hydrogen bonding with esters and lactones.

### Introduction

It was reported recently that the ring size has a marked effect on the donor ability of cyclic ethers in hydrogen-bonding.<sup>1b</sup> When account is taken of the electronic effects of substituents, it is found that the best donor ability is associated with the 4-membered ring, followed by the 5-, 6- and 3-membered rings in that order, the last being markedly poorer. Because of the structural similarity between lactones and cyclic ethers and because of the marked effect of ring size on other chemical properties of lactones, it seemed of interest to extend the hydrogen bonding studies to the 4-, 5- and 6-membered saturated lactones. In addition, the hydrogen-bonding of several esters and ketones was investigated for comparison with the lactones.

As in previous work in this series on hydrogen bonding, both a calorimetric method and a spectroscopic method were used to determine the relative donor abilities. The former involved the determination of the heat of mixing with chloroform,

and the latter that of the shift of the OD band in methanol-*d* solutions. The correlation of the two methods has been established, and so their use serves as independent checks.

### Experimental

**Apparatus and Methods.**—Infrared spectra were determined with a Beckman model IR-2T spectrometer. The spectroscopic method of measuring hydrogen bonding by means of comparing the position of the monomeric OD band in 0.1 molar solution of methanol-*d* in carbon tetrachloride with the position of the OD band in 1.0 molar solutions of methanol-*d* in various donor compounds has been described previously.<sup>1,2</sup> A lithium fluoride monochromator with fixed slits was used for scanning the region from about 2000 to  $2500\text{ cm.}^{-1}$ , and the position of the bonded OD band was determined by subtracting the absorption of the pure compound from the absorption of the 0.1 molar methanol-*d* solution in that compound. Since the bands were quite symmetrical, the position of maximum absorption was taken as the band center.

For the investigation of the shifts of the relatively intense carbonyl and alkoxy bands, the compounds studied were dissolved in 10 parts by volume of carbon tetrachloride and the methanol or chloroform was present in approximately equimolar amounts with the donor compounds. A rock salt monochromator was used here. The band centers were

(1a) Department of Chemistry, Kansas State College, Manhattan, Kansas.

(1b) S. Searles and M. Tamres, *THIS JOURNAL*, **73**, 3704 (1951).

(2) W. Gordy, *J. Chem. Phys.*, **7**, 93 (1939).

determined from the center of the band contour at about 50% of maximum absorption rather than at the less well defined band maximum.

All solutions containing a lactone and methanol were prepared immediately before use so that the results would not be complicated by ester formation and the bands observed did not change in intensity during the measurements.

The apparatus and method employed for the heat of mixing determinations were essentially as described by Zellhoefer and Copley<sup>3</sup> with the modifications previously made.<sup>1</sup> The heats of mixing of each lactone, ester, ketone and ether listed in Tables I and II are with an equimolecular quantity of pure chloroform.

**Materials.**— $\beta$ -Propiolactone (B. F. Goodrich Co.) was fractionally distilled under reduced pressure over sodium metal, b.p. 83° (45 mm.),  $n_D^{20}$  1.4117.  $\gamma$ -Butyrolactone (Cliffs-Dow Co.) was also purified by fractional distillation, b.p. 77° (12.7 mm.),  $n_D^{20}$  1.4351.  $\delta$ -Valerolactone was prepared by the catalytic dehydrogenation of 1,5-pentane-diol,<sup>4</sup> b.p. 94° (7 mm.),  $n_D^{20}$  1.4554. 1-Methoxybutanone-3 was prepared by addition of methanol to methyl vinyl ketone,<sup>5</sup> b.p. 136–139° (745 mm.),  $n_D^{20}$  1.3980. Methanol<sup>6</sup> was prepared by the method of Redlich and Pordes,<sup>6</sup> b.p. 65° (750 mm.). The other substances used were obtained from the best commercial sources available and were dried and fractionally distilled in the usual manner. The middle fractions, boiling points and refractive indices of which were in agreement with literature values, were employed.

### Results and Discussion

The heats of mixing of  $\beta$ -propiolactone,  $\gamma$ -butyrolactone and  $\delta$ -valerolactone, and the shift of the OD band in methanol-*d* solutions are given in Table I. The results indicate that the 6-membered ring is the best donor in hydrogen bonding and the 4-membered ring is the poorest, with the 5-membered ring intermediate. This order with respect to ring size is the reverse of that found with the cyclic ethers.

TABLE I

EFFECT OF RING SIZE ON HYDROGEN-BONDING OF LACTONES

Compound	Heat of mixing with CHCl <sub>3</sub> , 25°, cal./mole	OD band, cm. <sup>-1</sup> Position	Shift
CCl <sub>4</sub>		2688	Reference
$\beta$ -Propiolactone	167	2636	52
$\gamma$ -Butyrolactone	379	2600	88
$\delta$ -Valerolactone	565	2583	103

Lactones have two possible bonding sites—the carbonyl oxygen and the alkoxy oxygen. The fact that the ring-size effect is opposite to that observed with cyclic ethers suggests that the alkoxy oxygen is not principally involved in the hydrogen bonding. The situation with regard to the bonding site is similar to that in esters, where it does not appear to have been established which oxygen is chiefly involved. Comparison of structurally similar ethers and ketones (see Table II) suggests that an alkoxy oxygen is generally a slightly better electron donor than a carbonyl oxygen. When the two functional groups are present in the same molecule but separated by two carbon atoms, as in 1-methoxy-3-butanone, the donor ability is about the same as in methyl butyl ether and more than in acetone. In esters, however, the carbonyl and alkoxy groups will be

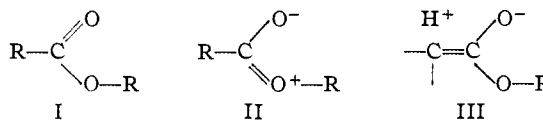
(3) G. F. Zellhoefer and M. J. Copley, *THIS JOURNAL*, **60**, 1343 (1938).

(4) L. E. Schniepp and H. H. Geller, *ibid.*, **69**, 1545 (1947).

(5) B. Puetzer, C. H. Nield and R. H. Barry, *ibid.*, **67**, 835 (1945).

(6) O. Redlich and F. Pordes, *Monatsh.*, **67**, 203 (1936).

modified by resonance involving such canonical forms as I and II (and III where there is an  $\alpha$ -hydrogen). This should decrease the relative



electron density on the alkoxy oxygen and increase it on the carbonyl oxygen, thus favoring hydrogen-bonding on the latter site.<sup>7</sup> The fact that esters are somewhat poorer electron donors than ketones may be attributed to the negative inductive effect of the alkoxy oxygen, which may compensate for the resonance effect.

TABLE II

HYDROGEN-BONDING WITH KETONES, ETHERS AND ESTERS

Compound	Heat of mixing with CHCl <sub>3</sub> , 25°, cal./mole	OD band, cm. <sup>-1</sup> Position	Shift <sup>a</sup>
Acetone	420	2610	78
Cyclohexanone	576	2590	98
Ethyl ether <sup>b</sup>	597	2593	96
Methyl butyl ether <sup>b</sup>		2594	95
1-Methoxy-3-butanone		2686	102
Methyl acetate	370	2637	51
Ethyl acetate	463	2637	51
Methyl propionate	435	2637	51

<sup>a</sup> CCl<sub>4</sub> solution reference (Table I). <sup>b</sup> Data taken from Reference 1.

The infrared spectra of methanol solutions of esters seem to confirm the carbonyl oxygen as the principal site of hydrogen bonding of esters and lactones. One might expect that the frequency of C=O and C–O vibrations would be altered when these groups are involved in hydrogen bonding. The idea was confirmed experimentally by observing that both the carbonyl band in simple ketones and the C–O–C band in ethyl ether are shifted to longer wave lengths when the compounds are dissolved in methanol.<sup>8</sup> When esters are dissolved in methanol or chloroform a similar shift is observed with the 5.7  $\mu$  band, assigned to the carbonyl vibration, but no significant shift could be detected in any of the bands in the region 8–12  $\mu$  where a C–O–C vibration may be expected. Likewise, a shift of the carbonyl band to higher wave lengths is observed with methanol solutions of the lactones

TABLE III

SHIFT OF C=O FREQUENCIES BY HYDROGEN-BONDING

Compound	C=O Frequency, cm. <sup>-1</sup> In CCl <sub>4</sub> soln.	In CCl <sub>4</sub> + CH <sub>3</sub> OH	Shift
$\beta$ -Propiolactone	1841	1834	7
$\gamma$ -Butyrolactone	1783	1771	12
$\delta$ -Valerolactone	1748	1733	15
Methyl acetate	1748	1740	8
Ethyl acetate	1742	1733	9
Methyl propionate	1743	1735	8
Acetone	1717	1711	6

(7) For evidence on the hydrogen bond as an electron density probe, see M. Tamres, S. Searles, E. M. Leighly and D. W. Mohrman, *THIS JOURNAL*, in press.

(8) The 1129 cm.<sup>-1</sup> in ethyl ether was shifted to 1123 cm.<sup>-1</sup>, and the carbonyl bands also are shifted by about the same amount; see Table III.

studied and the shift is roughly parallel to the degree of hydrogen-bonding. The fact that no other bands in the region 8–12  $\mu$  were shifted by more than 0.005  $\mu$  in chloroform solution indicates that bonding is not appreciable at any other site.

The marked effect of ring size on the hydrogen bonding of lactones seems explicable on the basis of the carbonyl group being the favored site. The resonance between forms I, II and III will be most favored by a bond angle of 120° between the carbonyl carbon and adjacent atoms, so that the carbon atom can use  $sp^2$  orbitals. When the carbalkoxy group is present in a 4- or 5-membered ring, a smaller angle is required, which results in an unsymmetrical arrangement of bond angles in contributing resonance forms of type II and III. Dampening of resonance between the two oxygens is consequently expected, reducing the gain in electron density of the carbonyl oxygen. The effect, of course, is greater for  $\beta$ -propiolactone than for  $\gamma$ -butyrolactone. Experimental evidence for the difference in the degree of resonance in the lactones is to be had in the carbonyl frequencies and in the dipole moments. As given in Table III, the carbonyl frequency increases in the order  $\delta$ -lactone <  $\gamma$ -lactone <  $\beta$ -lactone, indicating an increase in the rigidity of the carbonyl group. This effect of ring size on the carbonyl frequency has been of value in empirical data of ring size of lactones.<sup>9</sup> There also seems to be a greater resonance increment in the dipole moment of  $\gamma$ -butyrolactone than in that of  $\beta$ -propiolactone. With the assumption of no resonance interaction of the type occurring in ester, the molecular dipoles of the lactones have been calculated by vector addition of the carbonyl dipole of 2.8  $D$ <sup>10</sup> to the dipoles of 2.01  $D$

(9) L. Bauer, Ph.D. Thesis, Northwestern University, June, 1952.

(10) G. C. Hampson and R. J. B. Marsden, *Trans. Faraday Soc.*, **30**, Appendix p. 39 (1934).

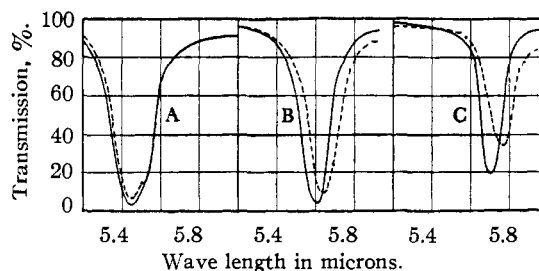


Fig. 1.—Effect of hydrogen bonding on carbonyl bands of lactones: A,  $\beta$ -propiolactone; B,  $\gamma$ -butyrolactone; C,  $\delta$ -valerolactone; solid lines, 10% solutions in carbon-tetrachloride; dotted lines, same with equimolecular amount of methanol added.

and 1.68  $D$  for the trimethylene oxide<sup>9</sup> and tetrahydrofuran,<sup>11</sup> respectively. Bond angles of 90 and 108° were used for the  $\beta$ - and  $\gamma$ -lactone rings, respectively. Both the calculated and measured<sup>12</sup> values for the  $\beta$ -lactone are 3.8  $D$ ; but for the  $\gamma$ -lactone the calculated dipole is 3.7  $D$  and that measured<sup>13</sup> is 4.12  $D$ . Much of this difference may be attributed to the added resonance in this compound.

If the above reasoning is correct, the same order with respect to ring size should be found for the basicity and donor ability in hydrogen-bonding of cyclic ketones. Work is under way to check this point.<sup>14</sup> We also hope to report on the ring-size effect in other similar systems, such as cyclic sulfoxides and amine oxides.

(11) H. D. Robles, *Rec. trav. chim.*, **58**, 111 (1939).

(12) T. L. Gresham, J. E. Jansen and E. W. Shaver, *THIS JOURNAL*, **70**, 998 (1948).

(13) R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1383 (1936).

(14) Hydrogen bonding measurements with cyclohexanone and cyclopentanone reported by W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **8**, 170 (1940), are in agreement.

EVANSTON AND URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE FLORIDA STATE UNIVERSITY]

### Azulenes. III.<sup>1</sup> An Attempted Synthesis of 1-Isopropyl-4,8-dimethylazulene. Migration of an Isopropyl Group

BY WERNER HERZ

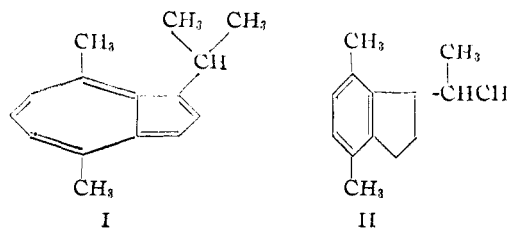
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Various routes leading to 1-isopropyl-4,7-dimethylindan were investigated. The usual diazoacetic ester method for the synthesis of azulenes, when applied to this indan, did not yield the expected 1-isopropyl-4,8-dimethylazulene (I), but vetivazulene. This is ascribed to migration of the isopropyl group from position 1 to position 2 of the azulene nucleus during or after dehydrogenation with palladium-charcoal.

1-Isopropyl-4,8-dimethylazulene (I) is of interest as an azulene which may be represented as having been formed by the combination of three isoprene units. This union is not of the "regular" or "head to tail" fashion usually found among terpenes of natural origin. However, it has been suggested<sup>2</sup> that "irregular" structures may well occur among azulenes derived from natural sources, inasmuch

(1) Paper II of this series, W. Herz, *THIS JOURNAL*, **74**, 1350 (1952).

(2) A. J. Haagen-Smit, "Azulenes, Fortschritte der Chemie Organischer Naturstoffe." Vol. 5, Springer Verlag, Vienna, 1948, p. 40.



as the number of apparently different azulenes isolated hitherto exceeds the number of "regularly"