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MASTER COPY

STRUCTURAL STUDIES BY NUCLEAR MAGNETIC RESONANCE. X. CONFORMATIONS OF ALIPHATIC ALDEHYDES.

by

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RELEASED FOR ANNOUNCEMENT
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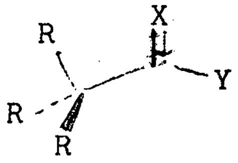
The spin-spin coupling constants between the aldehydic and α-protons of eighteen substituted acetaldehydes were studied as fuctions of temperature and solvent. Interpretation of the data in terms of conformations II and III, whereby a single bond eclipses the carbonyl group, lead to the conclusions:

(1) Monosubstituted acetaldehydes. In the absence of solvent when R is methyl, ethyl, n-propyl, n-amyl, isopropyl or phenyl the enthalpy difference, ΔH^0, between conformations II and III--excluding the statistical factor--is 800, 700, 600, 500 and about 300 cal/ mole in favor of III. When R. is t-butyl conformation II is more stable by 250 cal/mole. The ratio II/III increases with increase in solvent polarity, except for phenylacetaldehyde where it decreases. In the nonpolar solvents carbon tetrachloride and cyclohexane conformations II and III of phenylacetaldehyde are energetically equivalent.

(2) Disubstituted acetaldehydes. In the absence of solvent when both substituents are methyls the enthalpy difference between II and III--excluding the statistical factor--is 500 cal/mole in favor of III; when they are ethyls or t-butyls it is 250 and 1,100 cal/mole in favor of II. When only one of the substituents is methyl the more stable conformation has the methyl eclipsing the carbonyl; when neither substituent is methyl II is the more stable conformation. The ratio II/III increases with increase in solvent polarity.

(3) Cycloalkylcarboxaldehydes. When the ring is cyclohexyl, the enthalpy difference between II and III-- excluding the statistical factor--favors III by 400 cal/mole; when it is cyclopentyl, II is slightly more stable than III; when it is cyclobutyl, III is favored by about 150 cal/mole; and when it is cyclopropyl II is favored by about 1,500 cal/mole. Again the ratio II/III increases with increase in solvent polarity.

Several investigations have showed that the stable conformation of a tetrahedral carbon bonded to a trigonal carbon is I, whereby a single bond



I

(C-R) eclipses the C=X double bond. These include Raman and infrared studies on chloroacetone[3], haloacetyl halides[4,5] and N-methylchloroacetamide[6];

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(3) S. Mizushima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratani, I. Nakagawa, and N. Shido, J. Chem. Phys., **21**, 815 (1953).

(4) I. Nakagawa, I. Ichishima, K. Kuratani, T. Miyazawa, T. Shimanouchi, and S. Mizushima, ibid., **20**, 1720 (1952).

(5) A. Miyake, I. Nakagawa, T. Miyazawa, I. Ichishima, T. Shimanouchi, and S. Mizushima, Spectrochim. Acta, **13**, 161 (1958).

(6) S. Mizushima, T. Shimanouchi, I. Ichishima, T. Miyazawa, I. Nakagawa, and T. Araki, J. Am. Chem. Soc., **78**, 2038 (1956). The infrared spectra of α-halogenated carbonyl compounds [L. J. Bellamy, R. C. Thomas, and R. L. Williams, J. Chem. Soc., 3704 (1956); L. J. Bellamy and R. L. Williams, ibid., 4294 (1957)] and phenacyl ethers [P. Yates, S. Lipinski, and D. Vossius, Can. J. Chem., **39**, 1977 (1961)] have also been interpreted in terms of eclipsing conformations.

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microwave studies on acetaldehyde[7], propionaldehyde[8], acetyl chloride[9] and

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(7) R. W. Kolb, C. C. Lin, and E. B. Wilson, Jr., J. Chem. Phys., **26**, 1695(1957)

(8) S. S. Butcher and E. B. Wilson, Jr., ibid., **40**, 1671 (1964).

(9) K. M. Sinnott, ibid., **34**, 851 (1961).

propene[10]; electron diffraction studies on aliphatic ketones[11] and aldehydes[12];

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(10) D. R. Herschbach and L. C. Krishner, *ibid.*, **28**, 728 (1958).

(11) C. Romers and J. E. G. Creutzberg, *Rec. Trav. Chim.*, **75**, 331 (1956).

(12) L. S. Bartell, B. L. Carroll, and J. P. Guillory, *Tetrahedron Letters*, **13**, 705 (1964).

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and n.m.r. studies on propionaldehyde[13] and olefins[14-18].

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(13) R. J. Abraham and J. A. Pople, *Mol. Phys.*, **3**, 609 (1960).

(14) E. B. Whipple, J. H. Goldstein, and G. R. McClure, *J. Am. Chem. Soc.*, **82**, 3811 (1960).

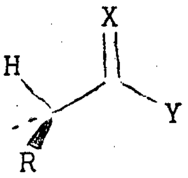
(15) E. B. Whipple, *J. Chem. Phys.*, **35**, 1039 (1961).

(16) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).

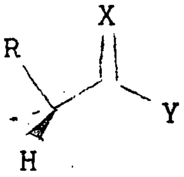
(17) A. A. Bothner-By, C. Naar-Colin, and H. Günther, *ibid.*, **84**, 2748 (1962).

(18) A. A. Bothner-By and H. Günther, *Disc. Faraday Soc.*, **34**, 127 (1962).

Some of our investigations have been directed towards elucidation of the relative stabilities of conformations II and III as functions of X, Y and R. In this paper we shall discuss the conformations of aliphatic aldehydes.



II



III

Results

Table I summarizes the coupling constants between the aldehydic proton and the α-protons of several aliphatic aldehydes. All values are averages of several measurements with a precision of ± 0.03 c.p.s. To insure accuracy and internal consistency values were always checked against the coupling of acetaldehyde, 2.85, 288 and 2.90 c.p.s. at 36°, 0° and -30° respectively.[19]

The coupling constants of monosubstituted acetaldehydes are smaller than that of acetaldehyde and increase with increase in temperature. Notable exceptions are t-butylacetaldehyde, whose coupling is larger than that of acetaldehyde and decreases with increase in temperature, and phenylacetaldehyde, whose coupling (in carbon tetrachloride) is independent of temperature. The couplings of disubstituted acetaldehydes vary extensively. When one of the substituents is methyl, the couplings increase with increase in temperature; when neither group is methyl they decrease. Cycloalkylcarboxaldehydes, except cyclopropylcarboxaldehyde, have small couplings. Those of cyclobutyl and cyclohexyl increase with increase in temperature; that of cyclopropyl decreases; and that of cyclopentyl is almost temperature independent.

Table II summarizes the effect of solvent on the coupling constants of several aldehydes. Increase in solvent polarity increases the coupling, except for phenylacetaldehyde, whose coupling decreases with increase in solvent polarity, and acetaldehyde, whose coupling shows only small variations.

The relative stabilities of the various conformations of a substituted acetaldehyde can be qualitatively assessed from the dependence of its coupling on temperature. Assuming $J_t > J_g$, where J_t is the trans coupling (dihedral

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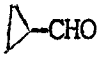
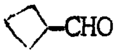
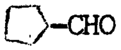
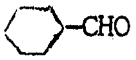
(19) These values are consistent with those reported in ref. 13 and by J.G. Powels and J. H. Strange, Mol. Phys., 5, 329 (1962).

Table I

Spin-Spin Coupling Constants[a], in C.p.s., of Aldehydes

Aldehyde	J_{CHCHO}			
	-30°	0°	36°	70°
CH_3CHO	2.90	2.88	2.85	
$MeCH_2CHO$	1.06	1.22	1.31	
$EtCH_2CHO$	1.42	1.53	1.69	1.80
$\underline{n}PrCH_2CHO$	1.51	1.60	1.75	1.80
$\underline{n}AmCH_2CHO$	1.48[b]	1.56	1.73	1.78
$\underline{i}PrCH_2CHO$	1.81	1.88	1.92	2.05
$\underline{t}BuCH_2CHO$	2.95	2.94	2.92	2.84
$C_6H_5CH_2CHO$	2.40[b]	2.40[b]	2.18 (2.40)[b]	2.20, 2.24[e]
$(Me)_2CHCHO$	1.01	1.12	1.17	1.35[d]
$(Et)_2CHCHO$	2.52	2.35	2.36	2.25
$(\underline{t}Bu)_2CHCHO$	6.20[b]		6.00[b]	5.75[b]
$Me(Et)CHCHO$	1.56	1.60	1.67	1.70
$Me(\underline{n}Pr)CHCHO$	1.45	1.59	1.76	1.75
$Me(C_6H_5)CHCHO$	1.07	1.25	1.31	1.45
$Et(\underline{n}Bu)CHCHO$	2.70[b]	2.55	2.52	2.35
	6.14	5.95	5.75	5.35
	1.72		1.82	
	2.11	2.12	2.12	2.05
	0.92	1.03	1.14	1.15

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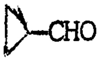
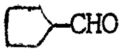
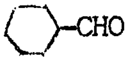
[a] Unless otherwide denoted all coupling constants are those of neat solutions.

[b] About 10% solution in carbon tetrachloride. [c] Value at 50°. [d] Value at 60°.

[e] Value at 90°.

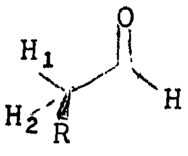
Table II

Solvent Effects on J_{CHCHO} of Aldehydes

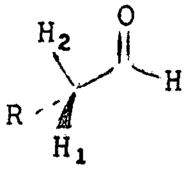
	J_{HH}(c.p.c.)[a]		
Aldehyde	Cyclohexane	Nitrobenzene	Acetonitrile
CH_3CHO	2.79	2.83	2.87
$MeCH_2CHO$	1.25	1.30	1.33
$\underline{t}BuCH_2CHO$	2.80	2.93	3.05
$(Et)_2CHCHO$	2.25	2.40	2.55
Me(Et)CHCHO	1.63	1.70	1.78
Et($\underline{n}$Bu)CHCHO	2.40	2.60	2.70
	5.05	5.60	5.80
	1.97	2.15	2.30
	1.00	1.15	1.20
$C_6H_5CH_2CHO$	2.40	2.18	2.00

[a] All values are at 36°.

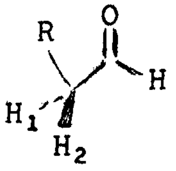
angle 180°) and J_g the gauche (dihedral angle 60°), the coupling should be temperature independent if IV_a, IV_b and V are energetically equivalent. If V is more stable than IVa, the coupling should increase with increase in temperature; and if less stable, it should decrease. Similarly, for disubstituted and cycloalkylcarboxaldehydes the coupling should be temperature independent if VI, VIIa and VIIb (also VIII, IXa and IXb) are energetically equivalent. If VIIa (R_1=R_2) is more stable than VI (also IXa more stable than VIII), the coupling should increase with increase in temperature; and if less stable, it should decrease.



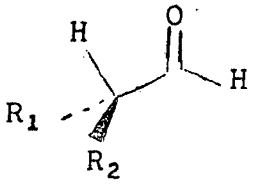
IV_a



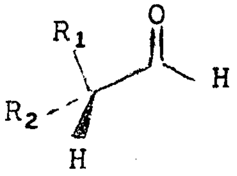
IV_b



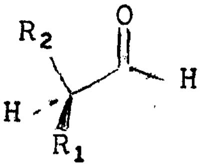
V



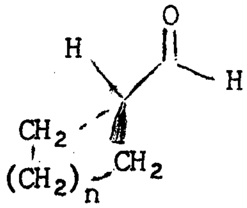
VI



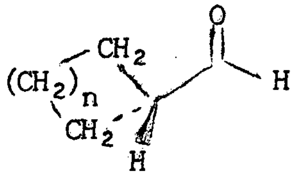
VIIa



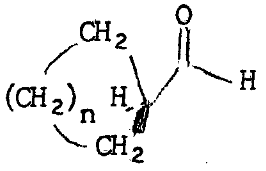
VIIb



VIII



IXa



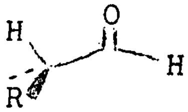
IXb

Table III summarizes percent populations of the various conformations of substituted acetaldehydes. Table IV shows their dependence on solvent. Values for monosubstituted acetaldehydes were calculated from equation (1).

$$J_{obs} = y(J_t + J_g)/2 + (1 - y)J_g \qquad (1)$$

Table III

Relative Population of Aldehydic Conformations[a]

	 (%)[b]			
Aldehyde	-30°	0°	36°	70°
$MeCH_2CHO$	23	31	34	
$EtCH_2CHO$	37	40	45	48
$\underline{n}PrCH_2CHO$	39	42	46	48
$\underline{n}AmCH_2CHO$	39[c]	41	46	47
$\underline{i}PrCH_2CHO$	48	50	51	55
$\underline{t}BuCH_2CHO$	80	79	79	77
$C_6H_5CH_2CHO$	65[c]	65[c]	65[c] (58)	66[c] (60)
$(Me)_2CHCHO$	19	20	21	23[d]
$(Et)_2CHCHO$	40	37	37	36
$(\underline{t}Bu)_2CHCHO$	92[c]		89[c]	85[c]
Me(Et)CHCHO	26	27	28	
Me($\underline{n}$Pr)CHCHO	25	27	29	
$Me(C_6H_5)CHCHO$	19	22	23	25
Et($\underline{n}$Bu)CHCHO	42[c]	40	40	37
—CHO	91	88	85	80
—CHO	28		30	
—CHO	34	34	34	33
—CHO	17	19	20	21

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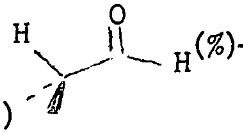
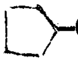
[a] Unless otherwise indicated these values are those of neat solutions.

[b] The remaining % corresponds to the conformation having the R group eclipsing the carbonyl. [c] About 10% solution in carbon tetrachloride. [d] Value from 60°.

Table IV

Solvent Effect on the Relative Populations of Aldehydic Conformations

	 (%)	
Aldehyde	Cyclohexane(36°)	acetonitrile(36°)
$MeCH_2CHO$	33	35
$\underline{t}BuCH_2CHO$	78	83
$(Et)_2CHCHO$	36	40
Me(Et)CHCHO	27	29
Et($\underline{n}$Bu)CHCHO	38	42
CHO	76	86
CHO	32	37
CHO	19	21
$C_6H_5CH_2CHO$	65	53

where y is the fractional population of IV and (1 - y) that of V; values for disubstituted acetaldehydes were calculated from (2), where y is the fractional

$$J_{obs} = yJ_t + (1 - y)J_g \qquad (2)$$

population of VI (also VIII) and (1 - y) that of VII (also X).

Calculation of these values required knowledge of J_t and J_g. Evaluation of J_t and J_g could be achieved as follows: Equation (3) expresses the

$$J_{obs} = 1/3\ (J_t + 2J_g) \qquad (3)$$

coupling of acetaldehyde and also of substituted acetaldehydes at very high temperatures (approach to free rotation), or at ordinary temperatures if it so happens that the various conformations are energetically equivalent. If we assumed that t-butylacetaldehyde exists exclusively in conformation IV, then equation (4) expresses its coupling. Combination of (3) -- using the

$$J_{obs} = 1/2\ (J_t + J_g) \qquad (4)$$

value of acetaldehyde -- and (4) gives J_t = 3.1 and J_g = 2.7 c.p.s. These values are obviously incorrect, since the coupling of di-t-butylacetaldehyde is 6.2 c.p.s. If we assumed that di-t-butylacetaldehyde exists exclusively in conformation VI, then J_t would have a value of 6.2 c.p.s. and J_g a value of 1.2 c.p.s. These values (6.2 and 1.2 c.p.s.) are lower and upper limits respectively.

A serious error arises from the assumption that J_t and J_g will be the same for acetaldehyde, monosubstituted acetaldehydes and disubstituted acetaldehydes. There is ample evidence in the literature that substitution of an alkyl group for a hydrogen decreases the coupling. For example, whereas the coupling of ethane[20] is 8.0 c.p.s., those of propane[21] and isobutane[22]

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(20) R. M. Lynden-Bell and N. Sheppard, Proc. Roy. Soc., Ser. A, 269, 385(1962).

(21) D. R. Whitman, L. Onsager, M. Saunders, and H. E. Dubb, J. Chem. Phys., 32, 67 (1960).

are 7.3 and 6.8 c.p.s. From electronegativity considerations[23] substitution of an alkyl group for a hydrogen should decrease the coupling by about 0.3 c.p.s. We can show that in aliphatic aldehydes each alkyl substituent decreases the average coupling, equation (3), by about 0.4-0.5 c.p.s. For example, whereas the coupling of acetaldehyde is 2.85 c.p.s., that of phenylacetaldehyde--temperature independent--is only 2.40 c.p.s.; and that of cyclopentylcarboxaldehyde--again temperature independent--is about 2.1 c.p.s. When the couplings of various disubstituted acetaldehydes are plotted against temperature, Fig. 1, the lines converge--for simplicity we have drawn straight lines--at high temperatures around 2.0 c.p.s. rather than 2.8 c.p.s.

In our calculation of percent population, therefore, we have used the following procedure to account for the fact that J_t and J_g for acetaldehyde, monosubstituted acetaldehydes and disubstituted acetaldehydes are different. Lower and upper limits of J_t of acetaldehyde can be estimated. For example, a lower limit of 7.0 c.p.s. (6.2 + 0.8) can be set from the highest coupling value of *di*-*t*-butylacetaldehyde. On the assumption that an alkyl group has no effect on the coupling, an 8.3 c.p.s. value was calculated from detailed temperature studies of the coupling of propionaldehyde.[13] Correction for the alkyl effect decreases this value to about 7.4 c.p.s. We have therefore chosen, somewhat arbitrarily, J_t of acetaldehyde as 7.6 c.p.s. and calculated J_g as 0.5 c.p.s. The data in Tables III and IV were calculated from these

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(22) J. S. Waugh and F. W. Dobbs, *ibid.*, **31**, 1235 (1959).

(23) R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, **7**, 165 (1963-64). See also R. E. Glick and A. A. Bothner-By, *J. Chem. Phys.*, **25**, 362 (1956).

values after correcting the observed coupling constants by 0.4 c.p.s. for each alkyl or aryl substituent.

Table V summarizes the enthalpy differences, calculated from plots of log K vs. 1/T, between individual conformations; e.g. V vs. IVa, VI vs. VIIa, and VIII vs. IXa (the statistical factor of two has been excluded). Table VI shows the effect of solvent on the free energy difference, at 36°, between such individual conformations. For disubstituted acetaldehydes where $R \neq R_2$ ΔH^0 and ΔF^0 values were calculated as if VIIa and VIIb were equivalent. Although such values have no physical significance they will be helpful in some later comparisons.

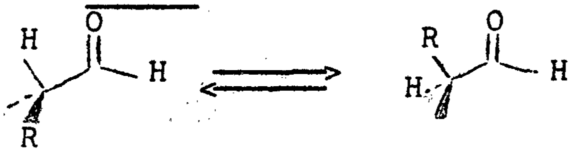
In addition to the experimental errors, the accuracy of the ΔH^0 values depends on the values chosen for J_t, J_g and substituent effect. To get an estimate on the accuracy of ΔH^0 values we have calculated them as functions of J_t, J_g and substituent effect. With substituent corrections of 0.3 and 0.5 c.p.s. they increase and decrease by about 5%. By changing J_t from 7.2 to 8.0 c.p.s. they vary by about ± 10%. An error of ± 20% therefore seems reasonable.

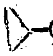
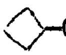
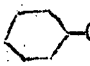
Discussion

Monosubstituted Acetaldehydes. When R is methyl, ethyl, n-propyl, n-amyl or isopropyl conformation V (alkyl eclipsing the carbonyl) is more stable than IVa or IVb (hydrogen eclipsing the carbonyl). The 800 cal/mole enthalpy difference between IVa and V when R is methyl is comparable to the 900 cal/mole difference obtained by microwave.[8] As anticipated, the enthalpy difference decreases as R increases in size, and becomes positive when R is t-butyl (IVa more stable than V).

The relative populations of V and IVa are solvent dependent. Increase in solvent polarity decreases the population of V; e.g. when R is t-butyl

Table V

ΔH° for 

Aldehyde	ΔH° (cal/mole)[a]
$MeCH_2CHO$	-800
$EtCH_2CHO$	-700
$\underline{n}PrCH_2CHO$	-600
$\underline{n}AmCH_2CHO$	-500
$\underline{i}PrCH_2CHO$	-400
$\underline{t}BuCH_2CHO$	+250
$C_6H_5CH_2CHO$	-300 (0^{b})
$(Me)_2CHCHO$	-500
$(Et)_2CHCHO$	+250
$(\underline{t}Bu)_2CHCHO$	$+1,100^{b}$
$Me(Et)CHCHO$	-200^{c}
$Me(\underline{n}Pr)CHCHO$	-200^{c}
$Me(C_6H_5)CHCHO$	-400^{c}
$Et(\underline{n}Bu)CHCHO$	$+300^{c}$
-CHO	+1,500
-CHO	-150^{d}
-CHO	~ 0
-CHO	-400

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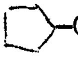
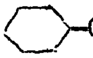
[a] Unless otherwise denoted these are values of neat solutions. [b] From about 10% solution in carbon tetrachloride. [c] These values were calculated as if $R_1 = R_2$. See text. [d] Calculated from only two temperatures.

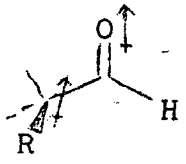
Table VI

ΔF^o_{36} for  as Function of Solvent

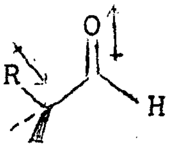
Aldehyde	ΔF^o_{36} (cal/mole)[a] cyclohexane	acetonitrile
$MeCH_2CHO$	-880	-820
$\underline{t}BuCH_2CHO$	+330	+550
$(Et)_2CHCHO$	+ 70	+180
$Me(Et)CHCHO$	-180	-120
$Et(\underline{n}Bu)CHCHO$	+130	+230
-CHO	+1,100	+1,560
-CHO	- 30	+ 90
-CHO	-480	-380
$C_6H_5CH_2CHO$	- 50	-340

[a] ΔF^o rather than ΔH^o is used because we did not study the temperature dependence of coupling in these solvents.

the population of V is 23% (cyclohexane) and 17% (acetonitrile). In terms of free energy, the ΔF^{o} between IVa and V becomes more positive (Table VI) in going from cyclohexane to acetonitrile. Such changes with solvent polarity are certainly reasonable, in view of the expected higher dipole moment of IV over V, as shown in X and XI. We want to point out, however, that the



X



XI

increase in J cannot be due solely to changes in the relative populations of IVa and V, as the coupling of acetaldehyde also increases--but only by about 2-3% -- in going from cyclohexane to acetonitrile.[24]

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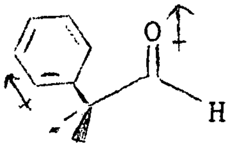
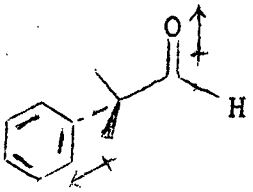
(24) A detailed discussion of coupling constant dependence on solvent will appear elsewhere.

Phenylacetaldehyde presents a sharp contrast to the alkyl monosubstituted acetaldehydes. Whereas in the nonpolar solvents carbon tetrachloride and acetonitrile IVa and V areenergetically equivalent, conformation V rather that IVa becomes more stable in the more polar solvents (in acetonitrile V is more stable than IVa by about 350 cal/mole). It seems reasonable that V should have a higher dipole moment than IVa (sp^2 carbon more electronegative than sp^3 carbon), as shown in XII and XIII. The greater effect of solvent



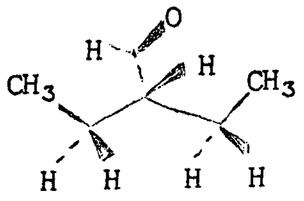
XII



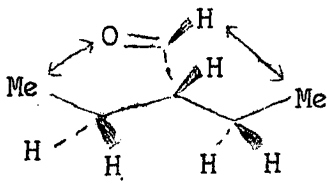
XIII

polarity on the ratio IV/V when R is phenyl than alkyl agrees with the greater contribution of phenyl over alkyl to the dipole moment of the aldehydic conformers.

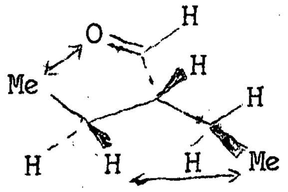
Disubstituted Acetaldehydes. Examining first the cases where $R_1 = R_2$ we conclude that when the alkyl groups are methyls VIIa is more stable than VI by 500 cal/mole; and when thay are ethyls or *t*-butyls VI is more stable than VIIa by 250 and 1,100 cal/mole. The interesting observation that conformation VI (hydrogen eclipsing the carbonyl) is more stable than VIIa (ethyl eclipsing the carbonyl) whereas V (ethyl eclipsing) is more stable than IVa (hydrogen eclipsing) merits some comment. This apparent inconsistency can be readily explained as follows: The most stable conformation of the ethyl groups when the hydrogen eclipses the carbonyl (VI) is XIV, whereby the alkyl chain is all-*trans* and completely staggered. If the alkyl chain were to be kept all-*trans* staggered in conformation VII, an 1,3-eclipsing methyl-proton interaction, and a less severe methyl-carbonyl interaction (XV), would result. Rotating to avoid these interactions leads to conformations XVa and XVb, which suffer from similar interactions. Consequently VI becomes



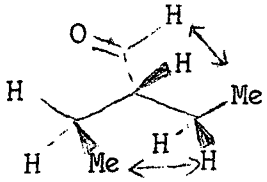
XIV



XV



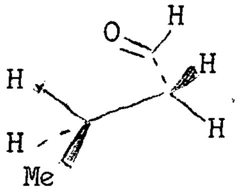
XVa



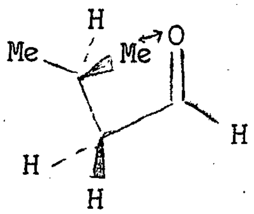
XVb

more stable than VIIa. In ethylacetaldehyde the isomer having the carbonyl eclipsing the ethyl group does not suffer from such interactions, as shown in XVI.

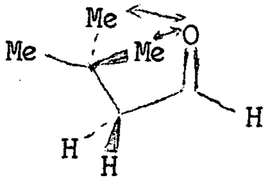
Of the two interactions shown in XV the 1,3-eclipsing methyl-proton interaction is probably the more severe and the one responsible in making



XVI



XVII



XVIII

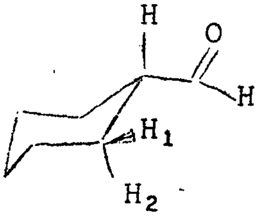
VIIa less stable than VI. That the methyl-carbonyl interaction cannot be the significant one is attested by the fact that when R is isopropyl V is more stable than IVa, although in V, as shown in XVII, such an interaction exists. Apparently two such interaction, as in t-butylacetaldehyde (XVIII), are sufficient to reverse the relative stability of the isomers.

When $R_1 \neq R_2$ the data afford the following firm conclusions: If R_1 = methyl and R_2 = ethyl or any alkyl, VIIa (methyl eclipsing) is the most stable conformation. VI (proton eclipsing) and VIIb (ethyl or other alkyl eclipsing) are practically energetically equivalent. The latter conclusion is drawn from the observation that ΔH^0 for these compounds, if R_1 is treated as equivalent to R_2, is about half that for dimethylacetaldehyde. If R_1 and R_2 are neither hydrogen nor methyl, then the most stable conformation is VI, apparently for the same reasons given for diethylacetaldehyde.

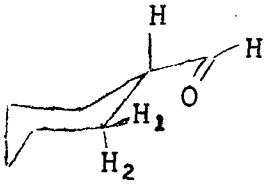
As with monosubstituted acetaldehydes the solvent effects are in accord with the proposed conformations; e.g. the ratio VI/VII increases with increase in solvent polarity, as VI should have a higher dipole moment than VII.

Cycloalkylcarboxaldehydes. The relative stabilities of VIII and IXa are very sensitive to ring size. Whereas IXa is more stable than VIII by 400 cal/mole when n = 3 (cyclohexyl), it is only slightly less stable when n = 2 (cyclopentyl), more stable by about 150 cal/mole when n = 1 (cyclobutyl) and finally less stable by about 1.5 Kcal/mole when n = 0 (cyclopropyl).

(a) **Cyclohexylcarboxaldehyde.** The finding that IXa (alkyl eclipsing the carbonyl) is more stable than VIII by about 400 cal/mole is as expected and supports the arguments advanced in the case of diethylacetaldehyde. In either conformation XIX or XX the alkyl chain is all-*gauche* staggered and



XIX



XX

the differences in interactions between XIV and XV are absent. Since in conformation XX the carbonyl is bisecting the H_1CH_2 angle, it is no surprise that cyclohexylcarboxaldehyde shows the same behavior as dimethylacetaldehyde.

(b) **Cyclopentyl- and Cyclobutylcarboxaldehyde.** The sharp contrast between cyclohexylcarboxaldehyde and either cyclobutyl- or cyclopentylcarboxaldehyde can be rationalized as follows: The ring puckering in cyclopentyl and cyclobutylcarboxaldehyde is certainly less than it is in cyclohexylcarboxaldehyde. Using the envelope form[25] for cyclopentylcarboxaldehyde

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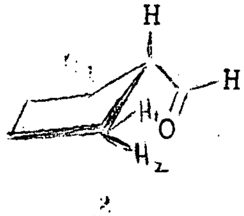
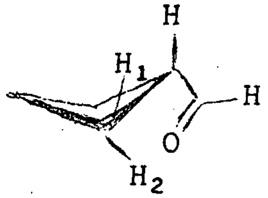
(25) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill Book Company, Inc., New York, 1962, p. 251.

it can be seen that in the isomer where the carbonyl is eclipsed by the carbon-carbon bond, the carbonyl is closer to H_2 (XXI) instead of bisecting the angle H_1CH_2 as in cyclohexylcarboxaldehyde. Apparently this proximity is sufficiently large to destabilize IXa to the extent that it is slightly less stable than VIII. The same argument can be applied to cyclobutylcarboxaldehyde (XXII).[26]



XXI



XXII

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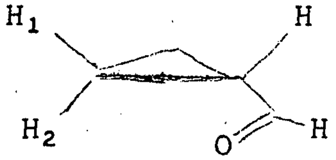
(26) It is reasonable to assume that the ring of cyclobutylcarboxaldehyde is puckered. For puckering of cyclobutyl rings see J. B. Lambert and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3710 (1963) and references cited therein. Although in these arguments we have used the aldehydic group in the equatorial or pseudoequatorial positions, analogous conclusions can be drawn from the conformations where the aldehydic group is axial.

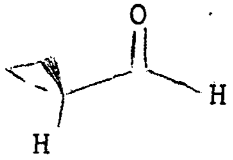
(c) **Cyclopropylcarboxaldehyde.** The complete reversal in cyclopropylcarboxaldehyde, VIII more stable than IXa by about 1.5 Kcal/mole, can be explained as follows: Extending the arguments used for cyclopentyl- and cyclobutylcarboxaldehyde it is evident that in IXa the carbonyl group eclipses H_2 (XXIII). This interaction apparently destabilizes IXa to such an extent



XXIII

that VIII becomes energetically favored. In addition, whatever factors force α, β- unsaturated aldehydes to assume the s-*trans* conformation,[27] may be responsible for the greater stability of VIII over IXa. We have certain reservations, however, regarding the magnitude of ΔH^0. In deriving this value we have assumed that J_t and J_g for cyclopropylcarboxaldehyde are the same as they are in other disubstituted acetaldehydes. Because of changes in angles and carbon hybridization in the cyclopropane ring this assumption is probably incorrect, and if J_t is larger than the values that we have used, then a more reasonable value for ΔH^0 may be 1 Kcal/mole rather than 1.5 Kcal/mole.

It was suggested[12] that in the gas phase cyclopropylcarboxaldehyde exists 50% in conformation VIII and 50% in conformation XXIV (carbonyl bisecting the



XXIV

cyclopropyl ring) rather than VIII and IX. Although our data do not permit an unequivocal choice between the two possibilities, on the basis of the following arguments conformations VIII and IX rather than VIII and XXIV seem more reasonable in the liquid phase.

Assuming VIII and XXIV as the only conformations, the coupling constant is expressed by equation (5), where y is the population of VIII and (1 - y) the

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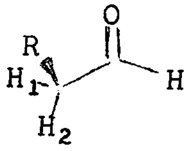
(27) J. A. Pople and T. Schaefer, *Mol. Phys.*, **3**, 547 (1960); Also A. A. Bothner-By, private communication.

$$J_{obs} = yJ_t + (1 - y)J_c \tag{5}$$

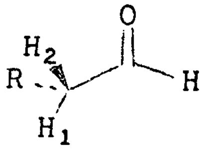
population of XXIV. From the strong dependence of J on temperature we draw the firm conclusion that in the liquid phase VIII and XXIV cannot be energetically equivalent. If J_t and J_c are comparable in magnitude--with J_t larger than J_c --then it is evident that VIII is more stable than XXIV. The large coupling constant of cyclopropylcarboxaldehyde is in agreement with VIII and XXIV, as both J_t and J_c should be large. What casts strong doubt on the whole argument, however, is the substantial decrease of the coupling with increase in temperature. Such a decrease requires J_c to be comparable in magnitude to J_g rather than J_t. Although such a possibility cannot be unequivocally excluded, it is highly improbable. We prefer therefore conformations VIII and IX rather than VIII and XXIV.

The variation of coupling constant with solvent polarity is again in accord with the higher dipole moment of VIII over IX.

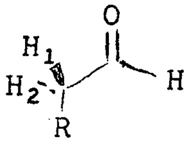
Consideration of Other Conformations. As we have showed our data are in good accord with eclipsed conformations. We wish to consider now bisecting conformations, XXV and XXVI for monosubstituted acetaldehydes and XXVII and XXVIII for disubstituted acetaldehydes. Equations 1, 2 and 3 become 6, 7 and 8



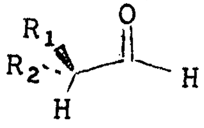
XXVa



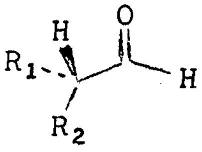
XXVb



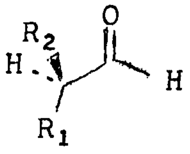
XXVI



XXVII



XXVIIIa



XXVIIIb

$$J_{obs.} \text{ (monosubstituted)} = y(J_c + J_{120^0})/2 + (1 - y)J_{120^0} \tag{6}$$

$$J_{obs.} \text{ (disubstituted)} = yJ_c + (1 - y)J_{120^0} \tag{7}$$

$$J_{obs.} = 1/3\ (J_c + 2J_{120^0}) \tag{8}$$

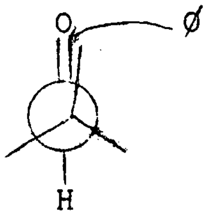
respectively, where J_c is the *cis* coupling and J_{120^0} the coupling when the dihedral angle is 120°. Since J_c should be comparable to J_t, and J_{120^0} comparable J_g, the data could be interpreted in terms of eclipsing conformations. We can, however, exclude these conformations on the basis of the following arguments:

(a) As mentioned, microwave and electron diffraction studies have showed that in the gas phase the stable conformations are eclipsing rather than bisecting. We see no good reason why in solution a reversal should occur.

(b) Since XXV and XXVII have higher coupling constants than XXVI and XXVIII one must conclude that increase in the size of R shifts the equilibrium in favor of XXV and XXVII. In terms of steric repulsions such a conclusion is highly improbable; *e.g.* models show that conformation XXVII of *di*-*t*-butylacetaldehyde is much more crowded than XXVIII.

(c) Since XXVI should have a higher dipole moment than XXV, and XXVIII higher than XXVII, increase in solvent polarity should decrease the coupling. Experimentally, however, the coupling increases with increase of solvent polarity.

Although we have interpreted our data in terms of eclipsing conformations, *i.e.* with the dihedral angle Ø as zero (XXIX), we want to emphasize that small



XXIX

variations in ϕ would not alter the interpretation of the results. This is a limitation of current understanding of spin-spin coupling and our results should not be construed as proof that the dihedral angle is zero. For accurate dihedral angle measurements one must rely on methods more accurate than n.m.r.

The causes responsible for making V more stable than IVa, even when R is isopropyl, are not well understood. Although the more favorable dipole-dipole interactions in V over IVa and the possibility of hydrogen bonding in V are plausible explanations, they cannot be the sole factors responsible for the greater stability of V, as witnessed by the case of phenylacetaldehyde. Very likely here are good examples of two interacting groups whose distance is in the attractive portion of the van der Waals curve.

Experimental

Except for *t*-butylacetaldehyde, *di*-*t*-butylacetaldehyde, cyclopropyl-, cyclobutyl- and cyclopentylcarboxaldehydes, all aldehydes used were freshly distilled samples of commercially available materials.

Di-*t*-butylacetaldehyde was prepared from *di*-*t*-butyl ketone.[28]

Cyclopropylcarboxaldehyde was prepared from cyclopropyl nitrile.[29] *t*-Butylacetaldehyde, cyclobutylcarboxaldehyde and cyclopentylcarboxaldehyde were prepared from the corresponding acids.[30]

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(28) M. S. Newman, A. Arkell, and T. Fukunaga, *J. Am. Chem. Soc.*, **82**, 2498 (1960).

(29) H. C. Brown and C. P. Garg, *ibid.*, **86**, 1085 (1964).

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(30) H. C. Brown and A. Tsukamoto, *ibid*., **86**, 1089 (1964).

N.m.r. Spectra were determined at 60 Mc. on a Model A-60 spectrometer.

Acknowledgment. We thank the United States Atomic Energy Commission for financial support, Grant COO-1189-14.