then absorb carbon monoxide from the solution to account for the observed octacarbonyl.

Experimental

Reduction of 2-Butenal.—A 0.30 *M* hexane solution of $HCo(CO)_4$ was prepared by disproportionation of $Co_2(CO)_8$ with N,N-dimethylformamide followed by acidification with HCl.[2] The resultant solution was washed with water and dried with anhydrous Na_2SO_4. A 20-ml. portion of the dry solution (6.0 mmoles of $HCo(CO)_4$) was injected into a 50-ml. round-bottom flask connected to a gas buret. The flask had a serum stoppered side arm and a magnetic stirring bar, and the whole system was under one atmosphere of carbon monoxide. The solution was stirred rapidly and 2.5 ml. (30 mmoles) of 2-butenal was injected. The disappearance of $HCo(CO)_4$ was followed by titration of 0.5-ml. samples withdrawn periodically.[4] When all the $HCo(CO)_4$ had been consumed, 12 ml. of a 0.5 *M* ether solution of triphenylphosphine was injected to convert all the cobalt to insoluble complexes. The resultant slurry was centrifuged and the supernatant solution was analyzed by vapor phase chromatography after standardization with the pure compounds expected as products. The analysis showed a yield of 2.4 mmoles of butanal and only a trace, if any, of butanol.

All of the reactions reported above were run in a similar manner. Some benzene was used as a solvent in the two reactions involving aromatic compounds (Table I).

Reaction of Allyl Ethyl Ether.—A 0.31 *M* octane solution of $HCo(CO)_4$ was prepared as described above and dried with anhydrous Na_2SO_4. A 27-ml. portion of the dry solution (8.4 mmoles of $HCo(CO)_4$) was injected into a 50-ml. round-bottom flask connected to a gas buret. The flask had a serum stoppered side arm and a magnetic stirring bar, and the whole system was under one atmosphere of carbon monoxide. The solution was stirred rapidly and 4.6 ml. (42 mmoles) of allyl ethyl ether was injected. After 6 min. all the hydrocarbonyl had been consumed and 0.6 mmole of gas had been absorbed. The cobalt compounds were removed as solids by adding 8.4 mmoles of triphenylphosphine and centrifuging. The supernatant solution was analyzed by vapor phase chromatography after standardization with pure ethyl propyl ether. This analysis showed a yield of 1.2 mmoles of ethyl propyl ether. Titration of the solution for aldehydes[16] indicated a yield of 2.5 mmoles of hydroformylation product.

The butyl vinyl ether reaction was performed in an analogous manner.

(16) J. S. Fritz, S. S. Yamamura, and E. C. Bradford, *Anal. Chem.*, **31**, 260 (1959).

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH., AND FROM MELLON INSTITUTE, PITTSBURGH, PENNA.]

Structural Studies by Nuclear Magnetic Resonance. II. Aldehyde 2,4-Dinitrophenylhydrazones

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The reaction of aliphatic aldehydes with 2,4-dinitrophenylhydrazine leads to *syn*-2,4-dinitrophenylhydrazones (DNP's). Prolonged standing of DNP solutions or the addition of acid effects *syn–anti* equilibrations; in all cases the *syn* isomer is thermodynamically favored over the *anti*. Several reported forms of acetaldehyde DNP which differ in melting point are all the *syn* isomer. Solvents capable of hydrogen bonding with N–H of the DNP increase the *syn–anti* ratio. Two N–H proton resonances appear in pyridine, dimethyl sulfoxide, and dimethylformamide solutions. The proton chemical shift and coupling constant data obtained on several aldehyde DNP's are discussed.

We have previously reported n.m.r. studies on the problem of structural isomerism in 2,4-dinitrophenylhydrazones (DNP's) and semicarbazones of various ketones.[2] α-Hydrogens *cis*[3] to the anisotropic group resonate at higher magnetic fields (shielded) than the corresponding *trans*-hydrogens; β- and γ-hydrogens *cis* to the anisotropic group resonate at lower magnetic fields (deshielded) than the corresponding *trans*-hydrogens. From the findings we determined the proportions of *syn* and *anti* isomers of these compounds in solution.

Extension of such studies to aldehyde DNP's appeared attractive for several reasons: (1) In aliphatic ketone DNP's the presence of only one set of aromatic proton resonances suggested that the various alkyl groups exert similar anisotropy effects on these aromatic protons. In this respect, comparison of alkyl groups with hydrogen seemed worthwhile. (2) Examination of molecular models indicated that the erstwhile aldehydic hydrogen *cis* to the aromatic ring should be deshielded relative to such a hydrogen occupying the *trans* position. (3) In solutions of acetaldehyde oxime the *anti* isomer is thermodynamically favored over the *syn*.[4] We anticipated reversal of the thermodynamic stability of the corresponding isomers of acetaldehyde DNP because of the large size of the 2,4-dinitrophenyl group. (4) Previous investigators have reported several forms of acetaldehyde DNP.[5,6] Ingold and co-workers[6] isolated two forms melting at 146° and 162°; Bryant[5] isolated three forms, m.p.'s 168.5°, 156–157°, and 149°. The latter investigator suggested that the 168.5° and 157° forms represented the stable and unstable isomers, respectively, and that the 149° form was a mixture of the two. Van Duin[7] isolated two isomers, m.p.'s 167–168° and 93–94°, to which he assigned *syn* and *anti* structures, respectively. On the basis of previous findings[2] we expected to be able to assign structures (*syn–anti*) to the various forms from n.m.r. studies.

The present study includes comments on the above points as well as discussions of new results, in particular those concerning long-range spin–spin couplings.

Results and Discussion

The proton n.m.r. spectra of several aldehyde DNP's (as dilute solutions in chloroform, methylene chloride, methylene bromide, acetone, dimethyl sulfoxide, dimethylformamide, pyridine, dioxane, tetramethylurea, and nitrobenzene) were examined at 60 Mc. For convenience we have adopted the numbering system shown in I.

***syn–anti* Isomerism.**—Table I summarizes the pertinent data on the isomeric compositions of several

(1) Mellon Institute, Pittsburgh, Pa.

(2) G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Am. Chem. Soc.*, **84**, 753 (1962).

(3) To make unequivocal the terminology used in this paper, note the following: The isomeric *forms* of the DNP of RCHO are denoted as (i) *syn* (in which H and the dinitroanilino group are on the same side of the C–N double bond) and (ii) *anti* (in which the groups are on opposite sides). The erstwhile aldehydic hydrogen in the *syn*-form is referred to as a *cis*-hydrogen (*i.e.*, *cis* to the dinitroanilino group), whereas the corresponding hydrogen of the *anti* isomer is referred to as a *trans*-hydrogen, etc.

(4) W. D. Phillips, *Ann. N. Y. Acad. Sci.*, **70**, 817 (1958).

(5) W. M. D. Bryant, *J. Am. Chem. Soc.*, **60**, 2814 (1938); **55**, 3201 (1933); **58**, 2335 (1936).

(6) C. K. Ingold, G. J. Pritchard, and H. G. Smith, *J. Chem. Soc.*, **70**, (1934).

(7) H. Van Duin, Thesis, Free University of Amsterdam, 1961.

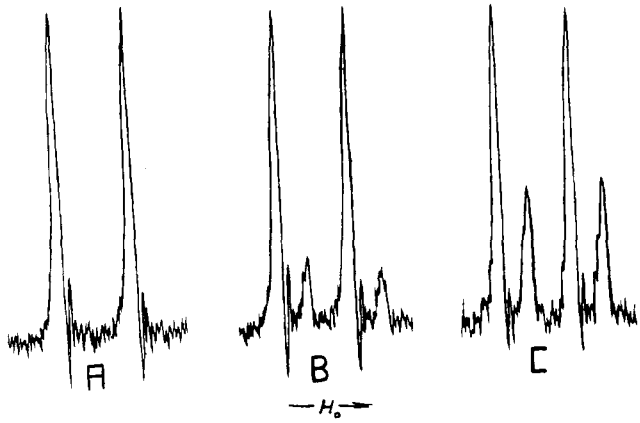
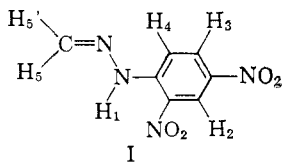


Fig. 1.—60-Mc. n.m.r. spectrum of the methyl hydrogens of acetaldehyde DNP in methylene bromide: A, freshly prepared solution; B, after 5 hr.; C, at equilibrium.

aliphatic aldehyde DNP's in solution. Freshly prepared solutions of these DNP's give spectra showing only one set of resonances, assigned to the *syn* (*i.e.*, *cis*-hydrogen) isomer for reasons which follow presently;



I

a new set of resonances attributable to the *anti* isomer begins to appear after several hours of standing at room temperature.[8] We shall discuss the case of acetaldehyde DNP in detail.

TABLE I

syn–anti COMPOSITION OF ALDEHYDE DNP'S IN SOLUTION

DNP	Solvent	Initial, % *syn*[a]	Initial, % *anti*	Equilibrium, % *syn*[a]	Equilibrium, % *anti*
Acetaldehyde					
M.p. 165–166°	CH_2Br_2	100	0	67	33
M.p. 165–166°	$C_6H_5NO_2$	100	0	66	34
M.p. 165–166°	Dioxane	100	0	75	25
M.p. 165–166°	Pyridine	100	0	79	21
M.p. 165–166°	Quinoline	100	0	73	27
M.p. 165–166°	Acetone-d_6	100	0	78	22
M p. 165–166°	DMF[b]	100	0	82	18
M.p. 165–166°	DMSO[c]	100	0	86	14
M.p. 160–161°	CH_2Br_2	100	0	67	33
M.p. 160–161°	$C_6H_5NO_2$	100	0	66	34
M.p. 160–161°	Pyridine	100	0	77	23
M.p. 145–146°	CH_2Br_2	>95	<5	66	34
M.p. 145–146°	Pyridine	>95	<5	80	20
M.p.[d] 87–105°	CH_2Br_2	15	85	67	33
Propionaldehyde	CH_2Br_2	100	0	78	22
n-Butyraldehyde	CH_2Br_2	100	0	85	15
Isobutyraldehyde	CH_2Br_2	100	0	95	5
Cyclopropanecarboxaldehyde	CH_2Br_2	100	0		

[a] *I.e.*, *cis*-hydrogen isomer. [b] Dimethylformamide. [c] Dimethyl sulfoxide. [d] Prepared by fractional crystallization of equilibrium mixtures from methylene bromide-heptane solutions. [e] We did not measure the equilibrium composition. All *syn*:*anti* ratios were determined by integration and are accurate to ±3%.

Acetaldehyde DNP.—As mentioned, several forms of acetaldehyde DNP differing in melting point have been reported. We were able to obtain forms melting at 145–146°, 157–158°, 160–161°, and 165–166°. These forms are the same isomer (with the exception of the 145–146°

(8) The statement does not include compounds capable of internal hydrogen bonding between H_1 and some group of the aliphatic part of DNP

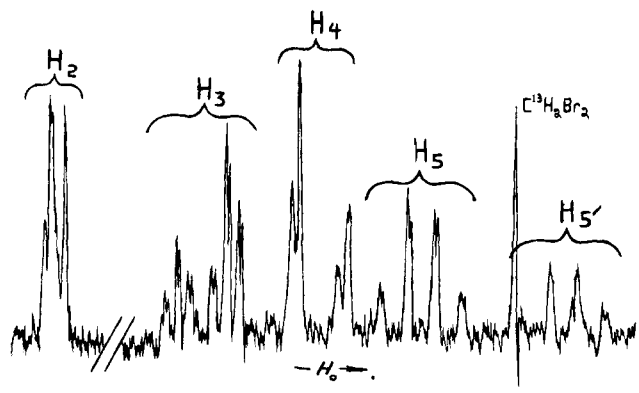


Fig. 2.—60-Mc. n.m.r. spectrum of the aromatic and "aldehydic" hydrogens of equilibrated acetaldehyde DNP in methylene bromide.

form which contains less than 5% of the other isomer) for the following reasons. Freshly prepared solutions give a methyl signal (at τ 7.90) which is one doublet of appearance appropriate for the M_3 part of an AM_3 system with J_{AM} = 5.5 c.p.s. and $J/\Delta\nu \cong 0.017$ (Fig. 1A). On standing at room temperature a second doublet appears (Fig. 1B), the ratio of the doublets becoming constant after one or more days (Fig. 1C). Concurrent with the appearance of the second doublet is the formation of a second "aldehydic" quartet (Fig. 2). On the basis of previous arguments[2] the original isomer is the *cis*-hydrogen. Equilibrium isomer ratios of the other aldehyde DNP's (Table I) support this assignment.

The *syn*:*anti* ratio is solvent dependent; it is two in methylene bromide and nitrobenzene, about four in pyridine, acetone, dimethylformamide, and tetramethylurea, and seven in dimethyl sulfoxide. Acid catalyzes the isomerization; methylene bromide solutions of acetaldehyde DNP prepared and recrystallized in the absence of acid[9] did not reach equilibrium after standing at room temperature for ten days; traces of sulfuric acid effected equilibration in less than a day. Conventionally prepared samples from either sulfuric or phosphoric acid solutions attained equilibrium within three days, with the lower melting samples equilibrating faster than the higher melting ones.

We were unable to isolate pure *anti* isomer. Fractional crystallization from methylene bromide–heptane solutions of the equilibrium mixture (67% *syn*–33% *anti*) of acetaldehyde DNP afforded crystals containing 85% *anti* isomer.

On the basis of these data we can make several comments: Formation of aliphatic aldehyde DNP's is kinetically controlled leading to *syn* isomers. The rate of *syn–anti* isomerization is slow enough to prevent formation of *anti* isomer during recrystallization. Traces of acid and *anti* isomer are the probable causes of observed variations in melting point of acetaldehyde DNP; we cannot exclude, however, differences in crystal structure as a possible cause. Van Duin's assignments are correct.

Chemical Shifts.—Table II summarizes the pertinent data on chemical shifts, which were computed by means of simple first-order analyses; sample calculations showed that the H_2 resonance is far enough from the resonances of H_3 and H_4 to affect only slightly the first-order separations of the lines of the latter hydrogens. The error involved in the relative resonance values is probably less than ±0.4 c.p.s.

(9) *Cf.* H. J. Shine, *J. Org. Chem.*, **24**, 252 (1959). Instead of diglyme as solvent for 2,4-dinitrophenylhydrazine we used the diethoxy analog. The DNP was precipitated by addition of water without any acid.

TABLE II

CHEMICAL SHIFTS (τ-VALUES[a]) OF ALDEHYDE DNP's[b]

Solvent	H_1	H_2	H_3	H_4	H_5	H_5'
			Formaldehyde DNP			
CH_2Br_2	−1.07	0.95	1.67	2.10	2.75	3.25
CH_2Cl_2	−1.12	0.92	1.65	2.22	2.80	3.25
$C_6H_5NO_2$	−1.08	1.10				
Dioxane	−1.12	1.02	1.67	2.12	2.73	3.30
Acetone	−1.32	1.02	1.60	2.00	2.42	3.17
Pyridine	−1.57	1.00				
DMSO[c]	−1.50	1.13	1.62	2.10	2.37	3.13
TMU[d]	−1.50	1.10	1.62	2.03	2.23	3.18
DMF[e]	−1.50	1.10	1.62		2.40	3.19
			Acetaldehyde DNP			
CH_2Br_2	−1.00	0.98	1.70	2.10	2.35	2.84
		(.93)[f]	(1.63)[f]	(2.08)[f]		
$CDCl_3$	−1.02	.92	1.73	2.10	2.40	2.88
		(.88)[f]	(1.70)[f]	(2.06)[f]		
Dioxane	−1.00	.98	1.70	2.17	2.37	2.72
		(.94)[f]	(1.63)[f]	(2.12)[f]		
$C_6H_5NO_2$	−0.97					
Pyridine	−1.43					
	(−1.14)[f]					
Acetone-d_6	−1.17	1.05	1.67	2.08	2.10	2.83
		(1.02)[f]	(1.62)[f]			
DMSO[c]	−1.23	1.20	1.72	2.20	2.07	2.78
	(−0.86)[f]	(1.14)[f]	(1.65)[f]	(2.17)[f]		
DMF[e]	−1.33	1.10	1.67			
	(−1.00)[f]	(1.06)[f]				
			Propionaldehyde DNP			
CH_2Br_2	−0.87	0.97	1.80	2.12	2.33	
			n-Butyraldehyde DNP			
CH_2Br_2	−1.00	0.97	1.70	2.12	2.37	
			Isobutyraldehyde			
CH_2Br_2	−0.98	0.95	1.68	2.10	2.40	
$CHCl_3$	−0.93	0.95	1.75	2.12		

[a] See G. V. D. Tiers, *J. Chem. Phys.*, **62**, 1151 (1958). [b] The concentration of DNP's varied from 2 to 8%; in dimethyl sulfoxide the concentrations were 12–15%. [c] Dimethyl sulfoxide. [d] Tetramethylurea. [e] Dimethylformamide. [f] Protons of the *trans*-hydrogen isomer.

In acetaldehyde DNP, the separation between the methyl resonances in the *syn* and *anti* isomers is solvent dependent, being 0.02–0.04 p.p.m. in dioxane, methylene bromide, chloroform, acetone, dimethylformamide, and nitrobenzene; 0.10 p.p.m. in pyridine; and 0.13 p.p.m. in quinoline. Two H_1 resonances appear in dimethyl sulfoxide, dimethylformamide, and pyridine; the resonance of the *syn* isomer is at lower field. In addition, the only hydrogen whose resonance changes appreciably with solvent is H_5. We have found[10] that acetone, dimethylformamide, dimethyl sulfoxide, and pyridine reverse the order of appearance of *syn*- and *anti*-methyl hydrogens of acetaldehyde DNP. These observations, coupled with the finding that the *syn*:*anti* ratio is higher in acetone, pyridine, dimethylformamide, and dimethyl sulfoxide than it is in methylene bromide and nitrobenzene, suggest that the former solvents stabilize the *syn* isomer with respect to the *anti* by hydrogen bonding with H_1. Steric considerations support this suggestion.

The resonance position of H_1 ($\tau \cong -1$) is insensitive to concentration and weakly solvent dependent. *o*-Nitrophenylhydrazones behave similarly; *m*- and *p*-nitrophenylhydrazones, however, show H_1 resonances that are strongly solvent dependent.[11] These results indicate the H_1 is intramolecularly hydrogen bonded to the *o*-nitro group. Good hydrogen-bonding solvents apparently compete with the *o*-nitro group for H_1.

(10) G. J. Karabatsos and F. M. Vane, unpublished results.

(11) F. M. Vane, unpublished results.

In the spectra of aliphatic ketone DNP's the presence of only one set of resonances for each aromatic hydrogen implies that methyl, ethyl, and propyl groups exert indistinguishable anisotropy effects on these hydrogens. Acetaldehyde DNP (Fig. 2) shows two sets of resonances for each aromatic hydrogen. We ascribe this finding either to solvation and conformational differences between the *syn*- and *anti*-aldehyde DNP isomers or to differences in anisotropies between C–H and C–alkyl.

Spin–Spin Coupling.—Table III summarizes the pertinent spin–spin coupling constant data on some aldehyde DNP's along with similar data on two ketone DNP's. Values were calculated on the basis of simple first-order splittings, and are accurate to ±0.1 c.p.s. as shown by sample calculations.

Several examples of long-range spin–spin couplings[12] are evident. Some of these (*viz.*, J_{23} and J_{24}) are merely unexceptional examples of *meta* and *para* couplings; the sizes observed are similar to many other known examples and do not merit further comment. However, some of the other couplings are

(12) Visible spin–spin couplings through more than three bonds are common in unsaturated compounds; *e.g.* (a) E. I. Snyder and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 1582 (1962); (b) G. S. Reddy, R. T. Hobgood, Jr., and J. H. Goldstein, *ibid.*, **84**, 336 (1962); (c) R. A. Hoffman and S. Gronowitz, *ibid.*, **83**, 3910 (1961); (d) R. A. Hoffman, *Mol. Phys.*, **1**, 326 (1958); (e) T. Schaefer, *J. Chem. Phys.*, **36**, 2235 (1962); (f) H. S. Gutowsky and A. L. Porte, *ibid.*, **35**, 839 (1961); (g) V. J. Kowalewski and D. G. de Kowalewski, *ibid.*, **36**, 266 (1962); (h) J. Martin and B. P. Dailey, *ibid.*, **37**, 2594 (1962).

TABLE III

SPIN–SPIN COUPLING CONSTANTS (J), IN C.P.S., OF ALDEHYDE AND KETONE DNP'S

DNP	Solvent	J_{12}	J_{13}	J_{14}	J_{15}	J_{15}'	J_{23}	J_{24}	J_{25}	J_{25}'	J_{34}	J_{35}	J_{35}'	J_{45}	J_{45}'	J_{55}'
Formaldehyde	CH_2Br_2	[a]	0.7	0.2	0.8	[a]	2.6	0.4	[a]	[a]	9.7	[a]	[a]	[a]	~0.2	11.0
Formaldehyde	Dioxane	[a]	.7	[e]	1.0	[a]	2.5	.4	[a]	[a]	9.8	[a]	[a]	[a]	[e]	11.3
Formaldehyde	Acetone	[a]	.7	[e]	0.8	[a]	2.6	.4	[a]	[a]	9.7	[a]	[a]	[a]	[e]	11.2
Formaldehyde	DMSO[b]	[a]	.7	[e]	0.8	[a]	2.6	.4	[a]	[a]	9.6	[a]	[a]	[a]	[e]	11.2
Formaldehyde	TMU[c]	[a]	[a]	[a]	[a]	[a]	2.6	.4	[a]	[a]	9.6	[a]	[a]	[a]	[e]	11.4
Formaldehyde	DMF[d]	[a]	[a]	[a]	[a]	[a]	2.6	.4	[a]	[a]	9.9	[a]	[a]	[a]	[e]	11.2
Acetaldehyde	CH_2Br_2	[a]	0.8		0.7	[a]	2.5	.4			9.8					...
Propionaldehyde	CH_2Br_2	[a]	.7		.7		2.6	.4			9.8					...
n-Butyraldehyde	CH_2Br_2	[a]	.7		.7		2.6	.4			9.9					...
Isobutyraldehyde	CH_2Br_2	[a]	.7		.6		2.5	.4			9.7					...
Acetone	CH_2Br_2	[a]	.7	0.3	...	...	2.5	.5	...	...	9.7	...	...	...	...	...
Diethyl ketone	CH_2Br_2	[a]	.7	0.2	...	...	2.5	.4	...	...	9.6	...	...	...	...	...

[a] $J \leqslant 0.1$ c.p.s. from observed line widths. [b] Dimethyl sulfoxide. [c] Tetramethylurea. [d] Dimethylformamide. [e] J was not determined; we estimate it to be 0.1 to 0.2 c.p.s.

unusual and seem worthy of discussion. The following remarks refer to the spectra of formaldehyde DNP unless otherwise specified.

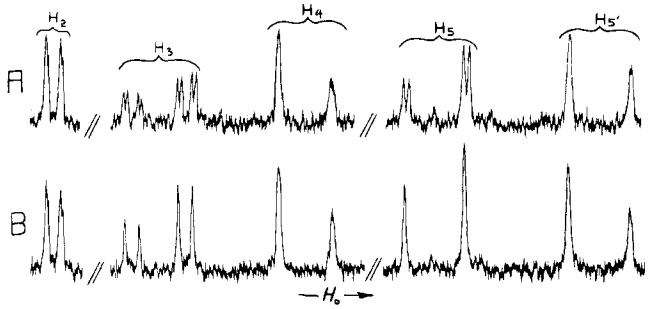


Fig. 3.—60-Mc. n.m.r. spectrum of formaldehyde DNP in methylene bromide: A, formaldehyde DNP; B, N-deuterioformaldehyde DNP.

H_1, although separated from both H_2 and H_3 by five bonds, shows a visible coupling only with H_3 (J_{13} = 0.7–0.8 c.p.s.); similarly, a J_{15} of 0.6–1.0 c.p.s. is seen while J_{15}' cannot be detected.[13] The spectra of undeuterated (Fig. 3A) and N-deuterated (Fig. 3B) formaldehyde DNP's are typical examples showing these differences. Although there is no visible J_{14} in the aldehyde DNP's, this coupling is clearly evident in the spectra of the two ketone DNP's, as is seen, for example, in the partial spectra of undeuterated (Fig. 4A) and N-deuterated (Fig. 4B) acetone DNP's.

H_4 shows a small (0.1–0.2 c.p.s.) coupling with H_5', but none with H_5. This can be seen from Fig. 3B and Fig. 4B. In 4B the *para* coupling is evident in both H_2 and H_4, in 3B only in H_2. The lines of H_4 (Fig. 3B) are broad (half-width 0.5 c.p.s.); similarly, the lines of H_5' are broader (half-width 0.4–0.5 c.p.s.) than those of H_5 (half-width 0.3 c.p.s.).

All couplings involving H_1 disappear in tetramethylurea and dimethylformamide. Apparently intermolecular exchange of H_1 is fast enough in these solvents to wash out these couplings.

The preferential coupling of H_1 with H_3 and not with H_2 emphasizes the importance of geometric considerations for the appearance of such couplings. The hydrogen bonding of H_1 with the *o*-nitro group places H_1 and H_3 in a *trans* coplanar conformation. Apparently such a conformation can enhance such a coupling[14]; 2,4-dinitrophenylhydrazine, 2-nitrophenylhydrazones, and other N-substituted 2,4-dinitroanilines also show this preferential coupling as do other aromatic systems. However, the appearance of a "zero" J_{15}' and a sizable J_{15} indicates that the steric requirements of such couplings are far from simple, since H_1 and H_5 cannot occupy such a *trans* coplanar arrangement.

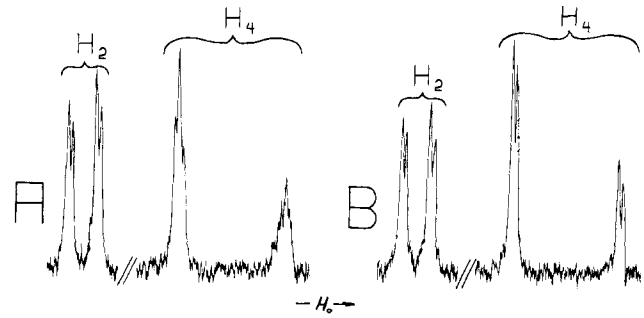


Fig. 4.—Partial 60-Mc. n.m.r. spectrum of acetone DNP in methylene bromide: A, acetone DNP; B, N-deuterioacetone DNP.

Finally it seems in order to comment on the large size of J_{55}' in formaldehyde DNP (11.0–11.4 c.p.s. in various solvents). For the analogous *gem*-H–H couplings in $H_2C{=}C\langle$ systems, a typical range of values which has been observed for a variety of substituents is from −3.5 to +2.5 c.p.s.[15] The large size of J_{55}' (as well as the observed values for J_{15} and J_{15}') in formaldehyde DNP suggests that markedly different factors are important in the two systems. Since no major differences in the H–C–H angle seem likely, it appears most probable at this early stage that electronic rather than steric factors are dominant. Further work in this area is in progress.

Experimental

Preparation of DNP's.—All DNP's were prepared according to well established procedures. They were recrystallized from ethanol–water and methanol–water mixtures. Whenever checked, *e.g.*, preparation of acetaldehyde DNP, preparations led to quantitative formation of DNP.

N.m.r. Spectra.—All n.m.r. spectra were determined at 60 Mc. on model A-60 spectrometers (Varian Associates, Palo Alto, Calif.), at a temperature of *ca.* 38°. The sample solutions were not degassed; it was found to be much more important (and adequate) in terms of obtaining optimum resolution and line widths to operate at the lowest possible radiofrequency levels. Tetramethylsilane was used as an internal reference. Line position, separations, and widths were read or measured directly from the spectral traces. Sample calculations referred to were run on an

(13) No information concerning the signs of any of the coupling constants reported is available from our experiments. Since the magnitudes of these long-range couplings are small, the possibilities must be considered that some of these J's have different signs and/or that a "zero" observed coupling constant is merely a fortuitous occurrence of a "cross-over" from one sign to the other.

(14) The generality and implications of this relationship in similar systems will be discussed elsewhere.

(15) C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

IBM 704 computer, making use of the FREQINT IV program kindly supplied by Dr. A. A. Bothner-By of Mellon Institute.

N-Deuterated DNP's were prepared by treating the DNP solution (in CH_2Br_2) with D_2O directly in n.m.r. sample tubes. The two-phase systems were shaken vigorously by hand for a few minutes at convenient intervals. The progress of the exchange could thus be readily followed by merely allowing the two phases to separate, the lower, organic phase being made long enough to keep the D_2O well above the critical region of the sample tube. Such equilibrations, run at room temperature without added catalysis, were usually complete in one or two days.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASH.]

The Nuclear Magnetic Resonance Spectra of Cyclopropane Derivatives[1]

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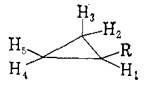
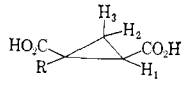
The n.m.r. spectra of cyclopropanecarboxylic acid, cyclopropyl bromide, and of 1-methyl and 1-phenylcyclopropane-*cis*-1,2-dicarboxylic acids have been analyzed. The spectral parameters are discussed in relationship to values found in other compounds.

The n.m.r. spectra of rigid molecules are of interest for two reasons. First, they permit an experimental correlation of chemical shifts and coupling constants with geometry, and this is of importance in testing theories dealing with these quantities. Second, the structural details of these compounds may often be determined for an analysis of the spectrum, particularly if the spectra of some model compounds are available. In order to obtain more data which may be useful in these connections, we have begun an investigation of some simple cyclopropane and cyclobutane derivatives. The results for some of the cyclopropane compounds are given here.

TABLE I

N.M.R. SPECTRA OF CYCLOPROPANE DERIVATIVES

Compound		Proton	Chemical shift, τ	Coupling constants, c.p.s. *cis*	*trans*	*gem*
	R = COOH	1	8.42	8.0(1, 2)	4.6(1, 3)	−4.3
		2(4)	9.03	10.5(2, 4)	7.5(2, 5)	
		3(5)	8.94	11.0(3, 5)		
	R = Br	1	7.16	7.3(1, 2)	3.9(1, 3)	−5.9
		2(4)	9.00	10.3(2, 4)	6.6(2, 5)	
		3(5)	9.12	10.0(3, 5)		
	R = C_6H_5	1	7.63	8.6(1, 2)	6.2(1, 3)	−5.2
		2	8.44			
		3	7.92			
	R = CH_3	1	8.02			
		2	8.77	8.2(1, 2)	6.3(1, 3)	−5.0
		3	8.32			

Monosubstituted cyclopropanes are of particular interest since they permit a determination of all of the coupling constants for the systems. However, the analysis of the resultant A_2B_2C spectrum is not readily accomplished without a knowledge of the approximate values of chemical shifts and coupling constants. The spectrum of cyclopropanecarboxylic acid may be simplified by preparing the α-deuterio derivative which will then give an A_2B_2 spectrum (Fig. 1). From the relative intensities, it was apparent that one of the coupling constants had a sign opposite to that of the others[3]; the spectral parameters were then easily found, giving at 60 Mc.[4]

$$\nu_A = 546.2 \text{ c.p.s.} \qquad \nu_B = 540.4 \text{ c.p.s.}$$
$$J_{AA'} \sim J_{BB'}\,(cis) = 11.0 \text{ c.p.s.} \qquad J_{AB}\,(gem) = -4.1 \text{ c.p.s.}$$
$$J_{AB'}\,(trans) = 7.0 \text{ c.p.s.}$$

It can be seen that the *cis* coupling constant is larger than the *trans* constant, as expected based on the dihedral angles involved.[5]

Approximate values for the coupling with the 2-proton of cyclopropanecarboxylic acid were easily obtained from the resonance bands corresponding to this proton. Using the above parameters and those for the 2-proton, it was possible to obtain the "best" parameters using an iterative program for an IBM-709 computer.[6] The values obtained for the 60-Mc. spectrum are given in Table I, and gave the spectrum shown in Fig. 2.[7] It was not possible to fit the spectrum if the *gem* coupling constant was taken as positive. In analogy with the relative magnitudes of the coupling constants for the A_2B_2 part, the larger of the constants, J_{AC} and J_{BC} was assigned as the *cis* constant and the smaller as the *trans* constant. Thus, the carboxyl group gives a larger chemical shift for the *cis*-hydrogens than for the *trans*-hydrogens.

Whereas the values of the vicinal coupling constants are in good agreement with those expected from the theoretical treatments of spin–spin coupling,[5,8] the values of the *gem* constants do not agree. The latter

(1) This work was supported by an A. P. Sloan Foundation fellowship to K. B. W.

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(3) This was easily seen by a comparison of the observed spectrum with those given in K. B. Wiberg and B. J. Nist, "Interpretation of N.M.R. Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962.

(4) The chemical shifts are given with respect to tetramethylsilane (600.0). The difference in shape of the two halves of the spectrum is presumably due to the difference between the *cis* and *trans* coupling constants between hydrogen and deuterium. We wish to thank Dr. R. Eisenthal for preparing the sample of cyclopropane-α-d_1-carboxylic acid used in this work.

(5) *Cf.* H. Conroy in "Advances in Organic Chemistry, Methods and Results," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, pp. 308–311.

(6) We wish to thank Drs. J. D. Swalen and C. A. Reilly for supplying us with this program. *Cf.* J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

(7) The spectrum was also obtained at 40 Mc., and an excellent fit was obtained using these parameters.

(8) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); M. Karplus and D. H. Anderson, *ibid.*, **30**, 6 (1959).