this[1] or similar[2] systems used nonpolar solvents such as hexane or benzene. Bäckström and Sandros observed that pure alcohols are poor solvents for energy transfer in benzophenone–biacetyl, probably due to the quenching effect[3] of alcohols on biacetyl.

In this work benzophenone and 4,4'-dimethylbenzophenone are the triplet donors and biacetyl is the acceptor. The solvents are hexane and mixtures of hexane and alcohols. The results are summarized in Fig. 1. It can be seen from the figure that a pro-
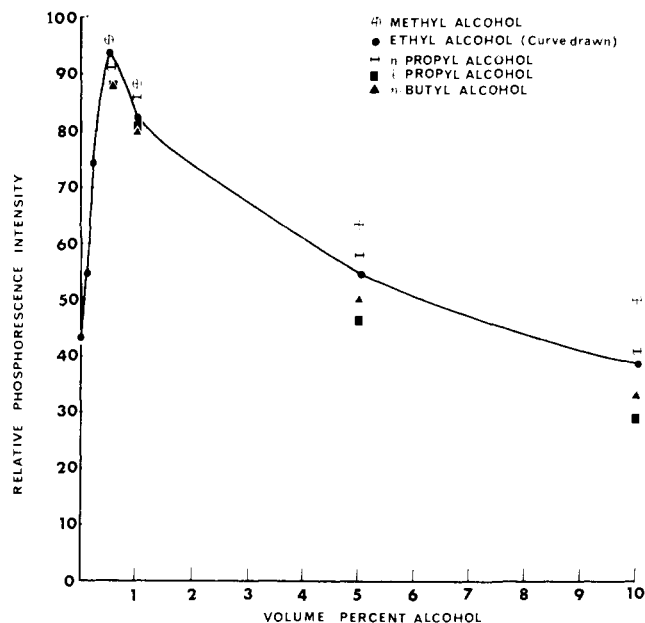

Fig. 1.—Biacetyl phosphorescence intensity (λ 524 mμ) at 25° vs. volume per cent alcohol in the hexane–alcohol solvent, λ_{EX} 366 mμ. Concentration of 4,4'-dimethylbenzophenone = 1.70 × 10^{-2} M; concentration of biactyl = 6.90 × 10^{-3} M. Curve drawn through ethyl alcohol points. Similar results are obtained for the benzophenone–biacetyl system.

nounced increase in biacetyl phosphorescence occurs with the addition of small amounts of alcohol to hexane. The maximum intensity is at about 0.5 vol. % of alcohol, and is more or less independent of the simple alcohols chosen. At high alcohol concentrations, the energy transfer becomes quite inefficient.

Since the donor benzophenones do not luminesce in fluid solutions at room temperature, phosphorescence spectra were obtained in rigid methylcyclohexane–isopentane and methylcyclohexane–isopentane–alcohol mixtures at 77°K. The results are shown in Fig. 2. Although the phosphorescence intensity continues to increase past the addition of about 1% alcohol, by far the most pronounced change in intensity occurs when less than 1% alcohol is added. Some emission shifts to shorter wave lengths are also. observed upon the addition of alcohol to these systems. No such pronounced effect is observed with biacetyl at low temperatures, and at room temperatures we have verified that alcohols quench[3] the biacetyl phosphorescence. Energy transfer from benzophenone to biacetyl is also markedly enhanced when small amounts of alcohol are added to methylcyclohexane–isopentane at 77°K., but will be reported at a later time.

(1) H. Bäckström and K. Sandros, Acta Chem. Scand., 14, 48 (1960).

(2) (a) J. Dubois and B. Stevens, "Luminescence of Organic and Inorganic Materials," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 115; (b) J. Dubois and M. Cox, J. Chem. Phys., 38, 2536 (1963); (c) J. Dubois and F. Wilkinson, ibid., 38, 2541 (1963).

(3) H. Bäckström and K. Sandros, Acta Chem. Scand., 12, 823 (1958).

Preliminary studies of biacetyl phosphorescence intensity vs. donor concentration show that the slopes of the curves are also increased when small amounts of alcohol are added to hexane. A study that remains to be performed is direct lifetime measurements of benzophenones in the presence of small amounts of alcohol.
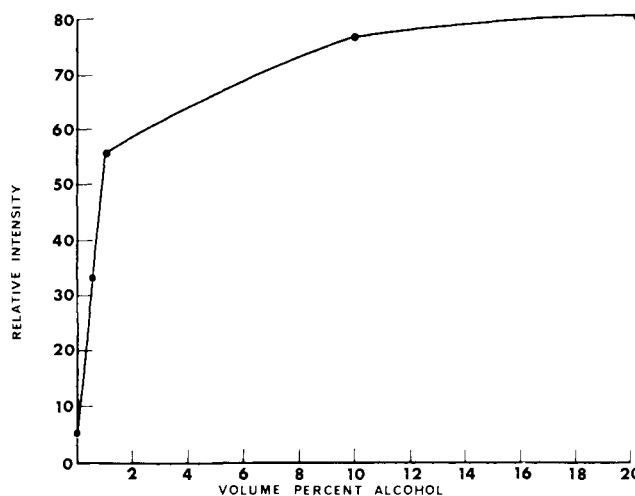

Fig. 2.—Relative phosphorescence intensity of 4,4'-dimethylbenzophenone at 77°K. vs. volume per cent alcohol in the methylcyclohexane–isopentane–alcohol solvent, λ (peak) 446–452 mμ, λ_{EX} 366 mμ. Concentration of 4,4'-dimethylbenzophenone = 1.70 × 10^{-3} M. Similar results are obtained for the benzophenone system.

An increase in the benzophenone lifetime associated with intermolecular hydrogen bonding would partially account for these results. Since the viscosity of the solvent increases upon addition of alcohol to hexane as does the amount of biacetyl quenching, the energy transfer efficiency must eventually decrease when the viscosity and quenching effects overcome the hydrogen bonding effect, since the process is at least partly diffusion controlled[4,2] in a fluid medium. Intermolecular hydrogen bonding may also impart some additional solution structure to the system, enabling energy transfer to occur over greater distances than the R_0 predicted by the Förster theory.[5] In those systems studied it appears that the major hydrogen bonding contribution is to the donor and not to the acceptor. Similar results are obtained with an isooctane–alcohol solvent system.

Further work is presently in progress on the above points.

(4) W. Melhuish, J. Phys. Chem., 67, 1681 (1963).

(5) T. Förster, Discussions Faraday Soc., 27, 7 (1959).

(6) Esso Educational Foundation Fellow, 1962–1963.

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Classification of Alcohols by Nuclear Magnetic Resonance Spectroscopy

Sir:

In the common n.m.r. solvents, deuteriochloroform and carbon tetrachloride, alcohols are often sparingly soluble, and their hydroxyl resonances are obscured by methylene and methyl resonances. The traces of acid always present in these solvents catalyze
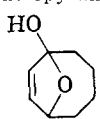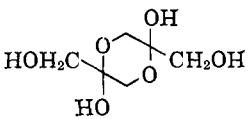
proton exchange so that spin–spin splitting of hydroxyl peaks is rarely observed. In dimethyl sulfoxide solution strong hydrogen bonding to the solvent shifts the hydroxyl resonance downfield (τ 6.0 or lower) and reduces the rate of proton exchange sufficiently to permit observation of hydroxyl proton splitting. Hydroxyl proton resonances in dimethyl sulfoxide lie below the low field C^{13} side band (221 c.p.s. at 60 Mc.) of the solvent. It is thus possible to use dimethyl sulfoxide[1] rather than the more expensive di-

TABLE I

HYDROXYL PROTON RESONANCES IN DIMETHYL SULFOXIDE

Compound[a]	Chemical shift, τ	Multiplicity[b]
Methanol	5.92	q
Ethanol	5.65	t
Isopropyl alcohol	5.65	d
t-Butyl alcohol	5.84	s
t-Amyl alcohol	6.01	s
Propylene glycol, 1-OH	5.55	t
2-OH	5.62	d
Cyclohexanol	5.62	d
cis-4-t-Butylcyclohexyl alcohol	5.89	d
trans-4-t-Butylcyclohexyl alcohol	5.55	d
Benzyl alcohol	4.84	t
Phenol	0.75	s
β-L-Arabopyranose, O–C–OH[c]	4.02	d
α-D-Glucopyranose, O–C–OH[c]	3.84	d
α-D-Fructopyranose, O–C–OH[c]	4.88	s

HO

(structure)

	4.88	s

OH

HOH₂C (structure) CH₂OH

	–CH₂OH	5.40	t
	–O–C–OH	4.45	s

HO

6β-Hydroxy-7β-methoxytropinone methobromide	4.00	d
10-Methyl-10-azatricyclo[4.3.1^{1,2}1^{2,5}]-undecan-8-ol	5.42	d
Haemanthamine	5.04	d
6-Hydroxycrinamine, 6-OH	3.92	d
11-OH	5.10	d
Tazettine	3.46	s
Deacetylbowdensine	5.15	d
	5.52	d
Androst-4-ene-3,17-diol	5.50	d
	5.58	d
18,20-Cyclopregn-5-ene-3,20-diol, 3-OH	5.44	d
20-OH	5.56	s
17α-Methylandrost-4-en-17β-ol-3-one	5.95	s
Androst-4-ene-3,17-diol 17-acetate	5.49	d
1,5-Cycloandrost-4-en-17-ol-2-one	5.60	d
Androsta-1,4-diene-17-ol	5.55	d

[a] All spectra were taken on dimethyl sulfoxide solutions with concentrations 10 mole % or less. [b] q = quarter, t = triplet, d = doublet, s = singlet. All splittings fall within the range 3.5–5.0 c.p.s. [c] Other hydroxyl protons (τ 5.0–5.9) show splitting but overlap to such an extent that specific assignments are not possible.

methyl sulfoxide-d_6. The hydroxyl proton in methanol gives a quartet (Fig. 1). Primary, secondary, and tertiary alcohols give clearly resolved triplets, doublets,

(1) Dimethyl sulfoxide (Crown-Zellerbach, Inc.) was stored over Linde Molecular Sieve 4A and used without further purification. No impurities other than water could be detected by n.m.r. Spectra were obtained with a Varian Associates HR-60 spectrometer. The probe temperature was 30°.
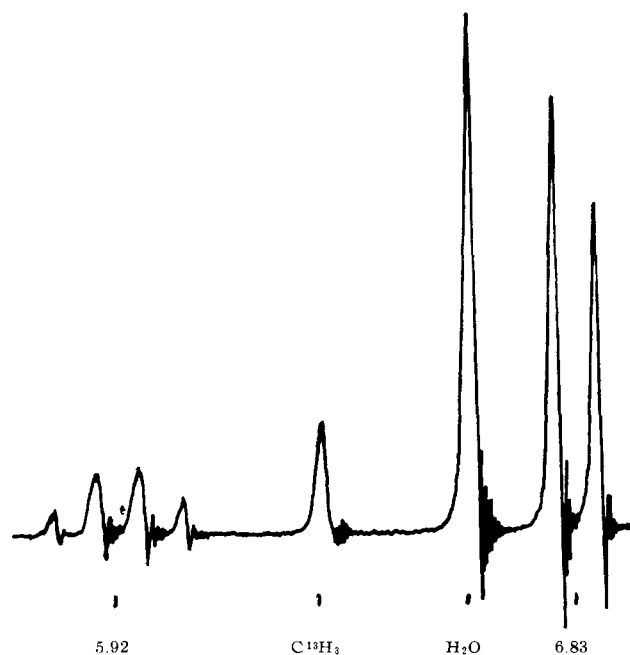

Fig. 1.—N.m.r. spectrum of methanol (5 mole %) and water (5 mole %) in dimethyl sulfoxide showing the independence of the methanol and water hydroxyl proton resonances and the splitting of the methanol hydroxyl proton. The lower field C^{13} side band of dimethyl sulfoxide (221 c.p.s. at 60 Mc.) is also shown.
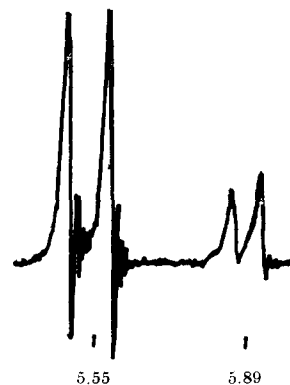

Fig. 2.—Hydroxyl proton resonances of a mixture of trans-4-t-butylcyclohexyl alcohol (77%) and cis-4-t-butylcyclohexyl alcohol (23%) in dimethyl sulfoxide.

and singlets, respectively. Water appears as a singlet above the low field dimethyl sulfoxide C^{13} side band. Polyhydroxy compounds give separate peaks for each hydroxyl proton. Addition of a few drops of deuterium oxide is sufficient to remove the hydroxyl hydrogens,[2] which can be identified even when superimposed on another multiplet. Strongly acidic or basic substances such as carboxylic acids, phenol, triethylamine, morpholine, and cyclohexylamine remove the hydroxyl splitting in methanol by exchange but pyridine and aniline do not. The method, however, is applicable to many alkaloids (see Table I). Very basic alkaloids may be run as the quaternary salts. The method should be especially useful for steroids and terpenes since few protons in such compounds give resonance lines in the τ 4.5–6.0 region. The method shows

(2) Hydroxyl exchange in dimethyl sulfoxide is slow relative to the nuclear spin inversion but is still rapid enough to permit complete exchange of hydroxyl protons for deuterons in a few minutes. Hydroxyl splitting in dimethyl sulfoxide has been observed independently: D. E. McGreer and M. M. Mocek, J. Chem. Educ., 40, 358 (1963).

promise in detecting conformational differences. The axial and equatorial hydroxyl groups in a commercial mixture of *cis*- and *trans*-4-*t*-butylcyclohexyl alcohols (Fig. 2) are clearly distinguished with the equatorial hydroxyl resonance at lower field, permitting quantitative analysis of the mixture. Hemiacetal and hemiketal hydroxyl protons appear as doublets and singlets, respectively, at lower field (τ 3.5–5.0) than ordinary hydroxyl protons.

The position of an alcohol hydroxyl resonance in dimethyl sulfoxide is almost independent of concentration below 25 mole % (concentration studies have been carried out on methanol, ethanol, 2-propanol, and *t*-butyl alcohol). Spectra of most medium and large molecules are run at concentrations far less than 20 mole %.

Acknowledgment.—We are grateful to Prof. W. C. Wildman for the alkaloid samples used in this study.

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The Structure of $C_2B_5H_7$

Sir:

Results pertinent to the structure of one of the recently synthesized carboranes, 2,4-dicarbaheptaborane,[1] are reported. This molecule has the form of a pentagonal bipyramid with two nonadjacent carbon atoms located in the pentagonal base, as shown in Fig. 1.
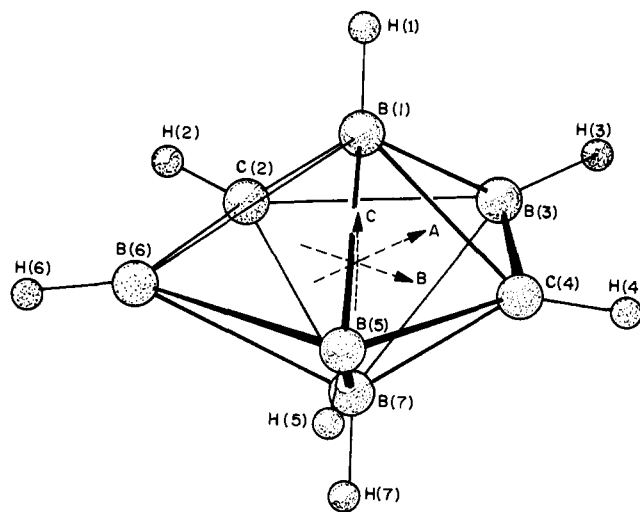

Fig. 1.—Molecular structure of 2,4-dicarbaheptaborane, $C_2B_5H_7$. Dotted arrows show orientation of principal axes. Bond distances are given in the text.

N.m.r. and infrared measurements[1] on this molecule have shown that there are no bridge hydrogen atoms and that there are two pairs of nonequivalent boron atoms. This information does not distinguish between three different structures. Chemical arguments favor a structure in which the two carbon atoms are nonadjacent.[1]

Standard microwave spectroscopic methods were used to obtain the results reported here. The five

(1) T. P. Onak, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **85**, 3378 (1963); R. Adams, *Inorg. Chem.*, **2**, 1087 (1963).

isotopic species which were analyzed were those present in a sample with the natural ^{10}B–^{11}B isotopic abundance. The five boron atoms have been located as accurately as this method allows,[2,3] and good approximate positions have been determined for the two carbon atoms. Thus the basic molecular skeleton is fairly well established.

TABLE I

CENTER OF MASS COORDINATES FOR
2,4-DICARBAHEPTABORANE SKELETON

(Atom numbers correspond to labeling in Fig. 1)

Atom no.	Mass, a.m.u.	Coordinates, Å.		
		A	B	C
1	11.012789	0.1346	0	1.1541
2	12.003804	0.3275	−1.2102	0
3	11.012789	1.3879	0	0
4	12.003804	0.3275	1.2102	0
5	11.012789	−1.1204	0.8254	0
6	11.012789	−1.1204	−0.8254	0
7	11.012789	0.1346	0	−1.1541

With the rotational constants obtained from the pure rotational spectrum analysis of the five isotopic carboranes, the coordinates of the five boron atoms can be computed with respect to a standard reference molecule, which in this case was chosen as the C_2-$^{11}B_5H_7$ molecule. The center of mass coordinates for the boron and carbon atoms are given in Table I. The position of the apical boron atom, B(1), which lies very close to the I_C axis, is poorly determined. By symmetry considerations, this atom lies in the AC plane, and may be either side of the BC plane by 0.1346 Å. From the present results one cannot distinguish between these two possibilities. If the a coordinate of this atom is positive then the B(1)–B(3) and B(1)–B(5) bond lengths are 1.704 ± 0.05 Å. and 1.894 ± 0.05 Å., respectively, whereas if the a coordinate is negative, then the corresponding bond lengths are 1.911 ± 0.005 Å. and 1.728 ± 0.005 Å. A B–B distance of 1.911 Å. is long compared to other boron compounds,[4–7] so the shorter boron distance is more probably correct.

In contrast to the uncertainty prevalent for the apical boron atoms, the locations of the ring boron atoms are well determined. Several assumptions are necessary in order to obtain the C–B bond lengths, however. Assuming values for the B–H and C–H bond distances, and assuming that these bonds are directed outward along the bisectors of the ring angles, the C and H atom positions can be fitted to the C_2-$^{11}B_5H_7$ observed rotational constants. Several values were assumed for the B–H distances and the carbon and hydrogen atom coordinates were refitted for each choice. The final B–H distances were chosen to reduce the difference between the calculated and observed moments of inertia to a minimum. The carbon atom position was insensitive to the B–H distance. All fitting was done such that both the carbon and hydrogen (C,H) atom positions could be varied simultaneously. The B(5)–B(6) bond distance was 1.650

(2) J. Kraitchman, *Am. J. Phys.*, **21**, 17 (1953).
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(6) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.
(7) W. E. Streib, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 2331 (1963).