TABLE I

N^{14} COUPLING CONSTANTS

Negative ion radical[a]	$\|a_N\|$, gauss
Nitroethane	25.2
1-Nitropropane	24.8
2-Nitropropane	25.4
1-Nitrobutane	24.3
2-Nitrobutane	24.5

[a] All generated in background electrolyte of 0.4 *M* KCl with 10% 1-propanol for solubility.

diphenylamine and several derivatives of chloropromazine has been carried out in aqueous buffers.

Acknowledgment.—We wish to express our appreciation to Robert Lorimer for aid in the design and construction of the electrochemical cells. This work was sponsored in part by the Atomic Energy Commission through contract AT(11-1)-686 and by the Air Force through AFOSR.

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RECEIVED JULY 10, 1961

ON THE MECHANISM FOR LONG RANGE PROTON SPIN COUPLINGS

Sir:

In a recent paper, Kreevoy, *et al.*,[1] question the evidence for hyperconjugation as a mechanism for long range coupling in unsaturated compounds[2] such as propargyl derivatives and suggest that α-hydrogen bonding[3] should be involved instead. They refer to recent theoretical work by Karplus[4] which, they claim, utilized essentially the α-hydrogen bonding model. This latter assertion is not valid. Though Karplus states explicitly[4] that "the orbitals on the protons H and H′ whose coupling is being determined are taken to be part of the sigma-electron system, this does not imply that hyperconjugation is not involved in his theory, since the proton spin coupling, as calculated by Karplus, is expressed in terms of hyperfine coupling constants and triplet state energies. Now the hyperfine coupling constants are obtained from e.s.r. data on related free radicals and insofar as the fragments H—C(—)—C(·) are concerned all theoretical interpretations[5,6] involve hyperconjugation either in its molecular orbital[5] or valence bond[6] formulation.

Thus the successful theoretical treatment of long range coupling[4] depends ultimately on hyperconjugation, rather than on the use of the α-hydrogen bonding model.

(1) M. M. Kreevoy, H. B. Charman and D. R. Vinard, *J. Am. Chem. Soc.*, **83**, 1978 (1961).

(2) (a) R. A. Hoffman, *Mol. Phys.*, **1**, 326 (1958); (b) E. B. Whipple, J. H. Goldstein and L. Mandell, *J. Chem. Phys.*, **30**, 1109 (1959); (c) E. B. Whipple, J. H. Goldstein and W. E. Stewart, *J. Am. Chem. Soc.*, **81**, 4761 (1959); (d) A. D. Cohen and N. Sheppard, *Proc. Roy. Soc. (London)*, **A252**, 488 (1959); (e) P. L. Corio and I. Weinberg, *J. Chem. Phys.*, **31**, 569 (1959; (f) R. A. Hoffman and S. Gronowitz, *Acta Chem. Scand.*, **13**, 1477 (1959).

(3) M. M. Kreevoy and H. Eyring, *J. Am. Chem. Soc.*, **79**, 5121 (1957).

(4) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

(5) (a) R. Bersohn, *ibid.*, **24**, 1066 (1956); (b) D. B. Chesnut, *ibid.*, **29**, 43 (1958).

(6) (a) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958); (b) P. G. Lykos, *J. Chem. Phys.*, **32**, 625 (1960).

Apparently[7] the fundamental difference between hyperconjugation and α-hydrogen bonding is that whereas hyperconjugation depends upon a non-vanishing magnitude for the exchange integral between a carbon pπ-orbital and the tetrahedral hybrid on an α-carbon, α-hydrogen bonding requires a non-vanishing magnitude for the exchange integral between the pπ-orbital and an α-hydrogen 1s-orbital.

Until calculations have demonstrated that acceptable estimates of the latter integral can account for the magnitudes and signs of observed long range couplings, it seems more reasonable to interpret these couplings in terms of hyperconjugation. More elaborate arguments and evidence in support of this view may be found in some recent works.[8]

(7) M. M. Kreevoy, *Tetrahedron*, **5**, 233 (1959).

(8) (a) R. A. Hoffman and S. Gronowitz, *Arkiv Kemi*, **16**, 471 (1960); (b) R. A. Hoffman, *ibid.*, **17**, 1 (1960).

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RECEIVED JULY 24, 1961

ON d HYBRIDIZATION IN CHLORINE

Sir:

The use of hybridization in valence bond theory in order to explain observed molecular geometries is well known. The classic example is of sp^3 hybridization in the group IV elements. In this case the bonding configuration (valence state) is considerably above the ground state in energy. The necessary promotion energy is regained upon bond formation yielding, of course, a stable molecule.

It is known that compounds of fluorine and chlorine exhibit many differences in structural properties. These differences frequently have been attributed to d hybridization in chlorine. Since chlorine has valence electrons in the 3s and 3p shells, excitation of these electrons to the 3d orbital has been assumed to be relatively easy in contradistinction to fluorine where the necessary excitation is 2s and 2p to 3d. The argument of easy orbital excitation when the principal quantum number remains unchanged is based in essence upon the assumption that the field in which the valence electrons move is reasonably close to coulombic.

In fluorine the energy of the center of gravity of states arising from $2s^22p^4$ (^{3}P)3d is 15.9 e.v.[1] Until recently the energy location of states arising from the configuration $3s^23p^43d$ in chlorine was unknown. Humphreys and Paul[2] and Minnhagen[3] have analyzed the chlorine spectrum. From their assignments the center of gravity of states arising from $3s^23p^4$(^{3}P)3d is 11.2 e.v.

In both fluorine and chlorine the excitation energy is large, in each instance being slightly less than 2 e.v. below the ionization limit. It would thus appear arbitrary to select the configuration of chlorine involving 3d electrons from the wealth of configurations near the ionization limit. In view of

(1) Charlotte E. Moore, "Atomic Energy Levels," Vol. I, United States Department of Commerce, 1949, Washington, D. C.

(2) C. J. Humphreys and E. Paul, Jr., *J. Opt. Soc. Am.*, **49**, 1186 (1959).

(3) L. Minnhagen, *ibid.*, **51**, 298 (1961).