activity has been found to be associated with the singly charged species[4] rather than with the un-ionized acid as in the present instance.

Acknowledgment.—We wish to express our appreciation to Professors Myron L. Bender and Harlan L. Goering for their comments and suggestions.

(4) T. Higuchi and H. N. Wolkoff, personal communication; T. Higuchi, A. D. Marcus and C. D. Bias, *J. Am. Pharm. Assoc., Sci. Ed.*, **43**, 129 (1954); M. L. Bender, *Chem. Revs.*, **60**, 85 (1960).

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OPPOSITE RELATIVE SIGNS OF GEMINAL AND VICINAL PROTON–PROTON COUPLING CONSTANTS IN SATURATED ORGANIC MOLECULES[1]

Sir:

Relatively few analyses of nuclear magnetic resonance spectra of the ABC classification have been reported.[2-6] Though the method of analysis is lengthy, it is a particularly sensitive means of obtaining the relative signs of coupling constants. We have analyzed the spectra of a series of substituted dioxolanes (I) (R = $-COO^-$ K^+, $-COOCH_3$, $-CD_2OH$, $-C_6H_5$, $-C(C_6H_5)_2OH$, $C(CH_3)_2-$ $OCO-$ $C_6H_4-p-NO_2$) for the purpose of obtaining information on the conformation of the dioxolane
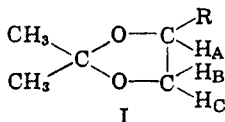
ring.[7] During this work we have found that the analyses require the geminal coupling constant to be of opposite sign to the vicinal coupling constants. This is a direct contradiction of the theoretical calculations of Gutowsky, Karplus and Grant,[4] and Karplus[8] unless it is assumed that the H–C–H angle in our compound is greater than 130°. The results of their calculations using valence-bond theory predicted vicinal coupling constants would be of the same sign as geminal coupling constants

(1) This research was supported by a grant to R. U. L. by the Corn Industries Research Foundation, Washington, and the calculations were performed by R. R. F. with the coöperation of the University of Ottawa Computing Center. We wish to thank W. G. Schneider for valuable discussions and M. Weinberger for aid in obtaining the spectrum at 24.3 Mcps.
(2) R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **31**, 996 (1959).
(3) C. A. Reilly and J. D. Swalen, *ibid.*, **32**, 1378 (1960).
(4) H. S. Gutowsky, M. Karplus and D. M. Grant, *ibid.*, **31**, 1278 (1959).
(5) S. Castellano and J. S. Waugh, *ibid.*, **34**, 295 (1961).
(6) C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).
(7) R. U. Lemieux, R. R. Fraser and J. D. Stevens, in preparation.
(8) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

when the H–C–H bond angle θ is less than 125°. This discrepancy points out the need for caution in assuming, as one might do on the basis of the theoretical work that all coupling constants are positive in saturated organic molecules and also in relating coupling constants to molecular wave functions.[9]

Throughout the series of compounds studied, estimated chemical shifts and coupling constants were adjusted by the iterative method as outlined by Banwell and Sheppard[6] using an IBM 650 computer until agreement was obtained in line positions with spectra measured on a Varian V-4302 spectrometer operating at 60 Mcps. Although there are, in theory, forty assignments possible for each ABC spectrum, each of the above compounds produced a spectrum with sufficient chemical shift between protons to make the combination bands relatively weak and easily identifiable. Thus, the number of alternative assignments was reduced to four. Of these, one is for the case where all three coupling constants, A_{AB}, A_{BC} and A_{AC}, are of the same sign. The other three assignments involve the cases where one of the three coupling constants is of opposite sign. Since absolute signs cannot be determined, the two vicinal coupling constants will be arbitrarily assigned a positive value for ease of discussion. The alternative possibility that in the dioxolanes the geminal coupling constant is positive and the vicinal coupling constants are negative is equally compatible with our data. For the spectrum of I with R = COO^-K^+, three sets of chemical shifts and coupling constants were found to give agreement in line position to within 0.15 cps. Unfortunately, convergence by the iterative procedure was not obtained for the set with A_{AC} negative. Nevertheless, only when A_{BC} had a negative value did the intensities of the calculated spectrum agree with the observed intensities to within ten per cent. (the limit of accuracy for peak height measurements). The parameters in this case were $\Delta\nu_B = 13.6$,[10] $\Delta\nu_C = 35.5$, $A_{AB} = 7.6$, $A_{BC} = -8.3$, $A_{AC} = 6.8$. With all coupling constants positive agreement required A_{BC} to be 7.4 cps. The assignment of protons B and C to the same carbon atom was established by exchange deuteration of the methyl ester using sodium ethoxide in O-deuterated ethanol followed by alkaline hydrolysis. The signal at low field was not present in the spectrum of the potassium salt of the 2-C-deuterated acid and the spectrum was a pair of doublets with spacing 8.2 ± 0.2 cps. This result obviously indicated that A_{BC} has a negative value. Confirmatory evidence that the vicinal and geminal hydrogens have coupling constants of opposite sign was obtained by measuring the spectrum of the compound at 24.3 Mcps. This spectrum is compared in Fig. 1 with the spectra calculated from the three sets of parameters which fit the 60 Mcps. spectrum except that the chemical shifts were reduced accordingly. Only with A_{BC} negative did all the line positions of the calculated spectrum agree within 0.2 cps. with those of the measured spectrum. It is therefore concluded that A_{BC} is negative.

The diphenylcarbinol derivative, R = $C(C_6H_5)_2-$ OH, whose 60 Mcps. spectrum differs greatly from

(9) M. Karplus, *J. Phys. Chem.*, **64**, 1793 (1960).
(10) $\Delta\nu_B = \nu_B - \nu_A$ is the chemical shift in c.p.s.
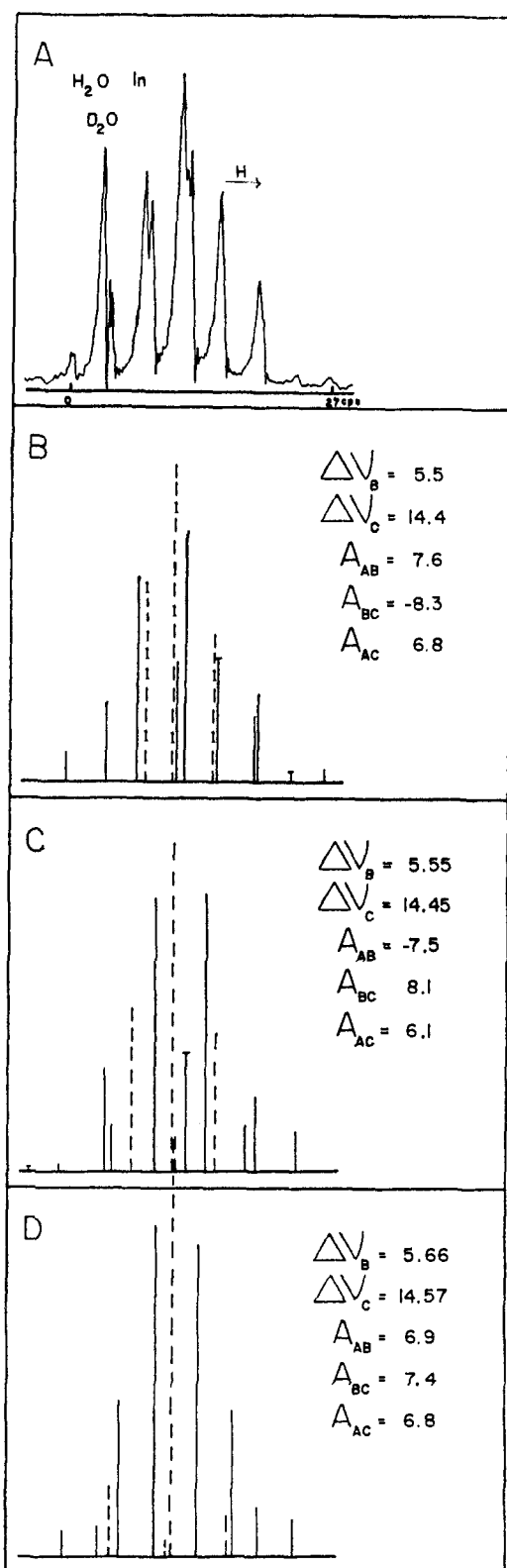
Fig. 1.—Experimental and calculated spectra for potassium 2,2-dimethyldioxolane 5-carboxylate: spectrum A was measured on a 15% solution in deuterium oxide at 24.3 Mcps. Spectra B, C and D were calculated using the parameters shown. A and C transitions are represented by solid lines, B transitions are represented by dashed lines,

and combination transitions by solid lines with the vertical bar. It should be noted that in A the two barely resolved transitions from nucleus C have intensities the opposite of that predicted in B. This discrepancy results from lack of sufficient recorder response, since the spectrum obtained by sweeping downfield gave a spectrum in which the intensities were reversed and in agreement with B.

that of the carboxylate salt, provides further confirmation of this conclusion. The spectrum of this compound at 24.3 Mcps. agreed to less than 0.2 cps. in line position with that predicted from the set of parameters with A_{BC} negative, which was obtained from the 60 Mcps. spectrum. There was no apparent disagreement in intensity. The other three sets of parameters gave predictions obviously in error, that is, greater than 500% in intensity and 1 cps. in line position. The theoretical spectra of the remaining four compounds measured at 60 Mcps. also agree best with the observed spectra when A_{BC} is negative. The generality of these findings is being investigated.

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THE DETECTION OF TRIPLET STATES BY THE CIS-TRANS ISOMERIZATION OF BUTENE-2

Sir:

Hammond, Leermakers and Turro[1] have suggested that it is possible to study the mechanism of various photochemical reactions by effecting the production of triplet intermediates from the reactants by using benzophenone, and other similar triplets, produced by photoexcitation as sensitizers.

As a means of elucidating reaction mechanisms the method suffers from the disadvantage that although the mechanism of the photosensitized reaction may be correctly understood, it does not of necessity follow that the same, or similar, mechanism applies to the unsensitized reaction.

A more reliable method would be to use a system in which the induced triplet intermediate of the original reaction undergoes an exchange in multiplicity with some other added species in accordance with the expression

$$T_1(\text{triplet}) + S_x(\text{singlet}) \longrightarrow S_1 + T_2 \qquad (1)$$
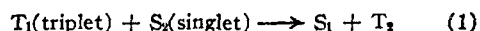
If a triplet intermediate is involved, this should suppress the reaction if the second triplet T_2 is comparatively unreactive. This type of transition should occur readily if the O–O transition, $T_1 \rightarrow T_2$, is exothermic. Usually, such interchanges can only be followed by phosphorescence or spectroscopic measurements.

The cis-trans isomerization of butene-2 through the triplet state provides a straightforward chemical means of following such excitation interchanges. Photosensitization studies in the vapor phase using mercury,[2] sulfur dioxide,[2] benzene[2,3] and a variety of other organic photosensitizers have shown that

(1) G. S. Hammond, P. A. Leermakers and N. J. Turro, J. Am. Chem. Soc., 83, 2395 (1961).

(2) R. B. Cundall and T. F. Palmer, Trans. Faraday Soc., 56, 1211 (1960).

(3) R. B. Cundall and D. G. Milne, to be published.