lar results in other cyclic and acyclic compounds.[22–25] As evident in Table II, the coupling of the ylide carbon is sensitive to isomer, larger in the trans isomers of **2**, **3**, and (trans by definition) **4**. The relative positions of the coupled atoms remain constant in both isomers, *i.e.*, no dihedral angle dependence. While no simple explanation of the stereospecificity is apparent, its utility can still be recognized as a means of isomer identification, particularly in those instances where the ^{1}H nmr methods are difficult or impossible.

Conclusions

The data reported here show clear and basic differences in molecular electronic structure among phosphorus ylides and triphenylphosphonium salts, although it appears that the electronic differences do not arise out of significant changes in the phosphorus bonding but primarily in the ylide carbon electronic nature. The triphenylphosphonium group has additive effects on ^{13}C shifts as a substituent although the directly bonded coupling to a coordinated carbon reflects changes in the electronic nature of that carbon in a rather complex way as a function of further substitution on that carbon. The ylide carbons in the apparently similar cyclopentadienyl and fluorenyl ylides are indeed of substantially different character with subsequently different degrees of localization of anionic charge. Ylides of the type $Ph_3PC(R)CO_2R'$ should not be considered to have primarily **b** type electronic character. Instead, they show greater localization, as exemplified by **c** type bonding.

Acknowledgments. I would like to thank Dr. Walter Creasy for help in purification of some of the compounds used in this work and also Dr. Dorothy Denny (Rutgers) for a gift of the triphenylphosphine oxide and tetraphenylphosphonium bromide.

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Selective Measurement of Nuclear Relaxation Times of Carbohydrate Derivatives[1]

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Contribution from the Department of Chemistry,
The University of British Columbia, Vancouver 8, British Columbia, Canada.

Received May 17, 1973

Abstract: The proton nuclear relaxation times (T_1 values) of 3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-bromo-2-deoxy-β-D-glucopyranose (**1**), of its α anomer (**2**), of the corresponding 2-chloro-gluco derivatives (**3**, **4**), and of the 2-bromo-α-D-manno derivative (**5**) have been measured by a Fourier transform method; the T_1 and T_2 values of some resonances of **1** and **3** were also measured *via* the audiofrequency pulse technique. Characteristic differences in T_1 values exist between protons having an axial or an equatorial disposition with respect to the ring system, and between vicinal protons that have a gauche interaction.

Although the phenomenon of nuclear relaxation is of fundamental importance to the measurement of nuclear magnetic resonance (nmr) spectra, it has been largely neglected by organic chemists.[5] There are many good reasons for this lack of interest, of which the most cogent is that until very recently, instrumentation suitable for the *routine* and selective measurement of the nuclear relaxation times of anything other than very simple molecules has been unavailable. However, the development of the selective, audiofrequency pulse (nmr) technique by Freeman and Wittekoek[6] and of Fourier transform methods by Ernst and Anderson, by Waugh and coworkers, and by Freeman and Hill[7] has made possible, at least in principle, relaxation studies of complex organic systems. Several laboratories, notably that of Allerhand,[8] have measured the longitudinal relaxation times of ^{13}C in natural abundance using Fourier transform methods, but few laboratories have shown much interest in equivalent studies of proton relaxation times. As part of a general program[9] to evaluate the very considerable potential of this area, we have chosen to study five pyranose derivatives which were known[10] to give reasonably simple proton nmr spectra. As will be seen, the audiofrequency pulse techniques does not satisfy entirely the selectivity

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(1) "Applications of Pulsed Nuclear Magnetic Resonance Spectroscopy," part 2. For part 1 see ref 9. For a preliminary communication see, *Carbohyd. Res.*, **27**, 286 (1973).

(2) Recipient of a National Research Council of Canada 1967 Science Scholarship, 1968–1971.

(3) Alfred P. Sloan Foundation Research Fellow, 1971–1973.

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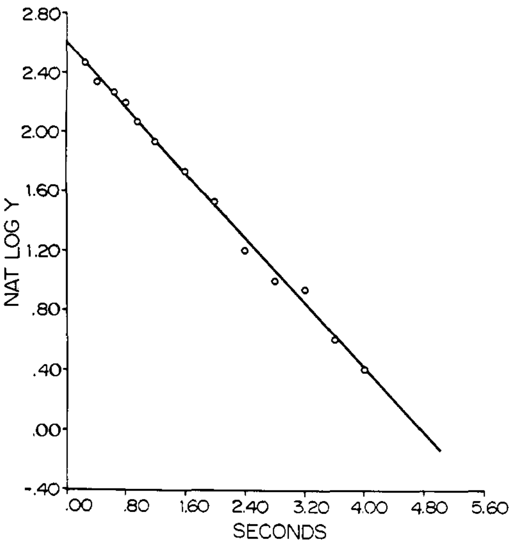


Figure 1. Copy of the computer output for the determination of the T_1 value for the downfield transition of the H-1 resonance of 3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-chloro-2-deoxy-β-D-glucopyranose (**3**). The input data are shown as open circles and the best least-squares fit is given as the straight line.

requirements for such molecules but does allow the facile determination of some T_2 values; on the other hand, the Fourier transform method allows for a far more general determination of T_1 values.

Experimental Section

All of the audiofrequency pulse measurements were made with an extensively modified Varian HA-100 instrument which has been described elsewhere.[6,9] Briefly, the required modifications and extra components are as follows.

(i) A frequency synthesizer (Hewlett-Packard, Model 5110 B) is used to provide the very stable audiofrequencies needed for the "lock" and "observe" channels of the spectrometer. It also provides the clock frequency for the "timer" used in ii below.

(ii) A pulse generator serves two purposes. First, it provides a rapidly responding switch (or gate) which can turn the "observe" channel on and off in response to signals from the second part of the unit, which constitutes a "timer." This latter unit can be programmed to give a series of pulse instructions to the gate and thereby to give a series of pulses to an appropriate part of the nmr spectrum.

(iii) A storage oscilloscope (Tektronix, Model R564B) is used to record the rapid, transient responses produced by the pulses of radiofrequency power. A permanent record of an experiment can be made with a modified Polaroid camera (Model 210).

These components can be incorporated into the main frame of the Varian spectrometer without any major alterations to the instrument, and thus the experiments can be performed routinely and without any hindrance to the normal function of the instrument. The requisite adjustments have been described previously.[6,9]

The Fourier transform determinations of T_1 were made with a Varian XL-100 instrument fitted with a Varian 620 L (16K) computer.

The following pulse sequence was used: delay–180°–*t*–90°–delay–90°.... The delay time was at least $4T_1$ and for the shorter relaxation times $10T_1$ delays were commonly used. The recovery times (*t*) were of the order of T_1. After Fourier transformation the spectra were plotted automatically. The T_1 values were obtained in a long hand and not very elegant manner. A mean base line was drawn through the noise and the height of each peak measured with respect to this datum line. These peak heights and the delay times (*t*) were used as the input for a computer program which plotted "ln (peak height)" *vs.* "*t*" and the least-squares fitted line. A typical example is given in Figure 1.

The samples of 3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-bromo-2-deoxy-β-D-glucopyranose (**1**), the corresponding α anomer (**2**), the corresponding 2-chloro derivatives (**3** and **4**), and the 2-bromo-manno derivative (**5**) were previously prepared by Dr. John Manville in this laboratory.[10] Recrystallization from aqueous ethanol gave pure samples of **1**, mp 161–162°; **2**, mp 112–113°; **3**, mp 160–161°; **4**, mp 153–154°; and **5**, mp 168–169°.

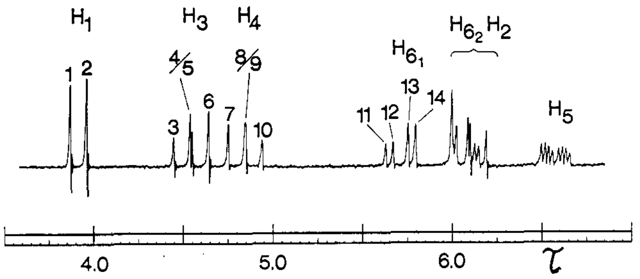


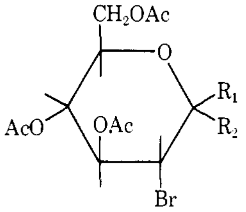
Figure 2. Partial ^{1}H nmr spectrum (Varian HA-100) of 3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-bromo-2-deoxy-β-D-glucopyranose (**1**) in deuteriobenzene solution (0.20 *M*) containing a small amount of acetone and TMS. A partial first-order assignment is given above the spectrum. Transitions of interest have been numbered for discussion in the text.

For the audiopulse experiments, the nmr solutions of **1** (0.20 *M*) and **2** (0.23 *M*) were made up in deuteriobenzene containing a small amount of TMS for a field-frequency lock and acetone for a pulse standard. It was hoped that the solution characteristics of each sample would be similar enough to allow comparison between them; the acetone was added to check this point (*vide infra*). Samples were filtered and then degassed (six freeze-pump-thaw cycles) prior to being sealed off to exclude oxygen.

Less concentrated solutions (0.1 *M*) were used for the Fourier transform experiments. For **2**, **3**, and **4** the concentrations were 0.1 *M*; for **1** the solution was 0.07 *M* due to lack of material; for **5** the concentration was just less than 0.1 *M* since some material failed to dissolve. These differences in concentration are probably the chief source of some of the minor inconsistencies of the T_1 values.

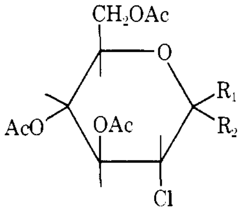
Results and Discussion

The five compounds **1–5** were chosen for this study



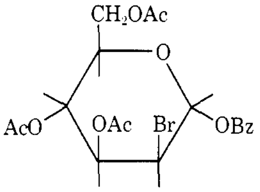
1, R_1 = OBz; R_2 = H

2, R_1 = H; R_2 = OBz



3, R_1 = OBz; R_2 = H

4, R_1 = H; R_2 = OBz



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because it was already known that they had well resolved ^{1}H nmr spectra and because they had approximately the same solution conformations. The normal ^{1}H nmr spectrum of **1** in solution is shown in Figure 2.

Initially, audiofrequency pulse experiments were performed on the clearly resolved H-1 doublet. Figure 3A shows photographs of two oscilloscope traces obtained during the measurement of T_1 on the upper field transition 2. Each photograph contains two pulse pairs with differing time delays. The π pulses at time zero have been superimposed (far left) and a single π/2 pulse has in turn been superimposed on them to check the values of M_0. In each photograph the

Figure 3. Copies of Polaroid photographs made during relaxation time measurements on transition 2 of derivative **1**. Duration of a $\pi/2$ pulse = 0.1 sec. (A) Each photograph contains two T_1 pulse pairs whose time zero π pulses have been superimposed. A simple $\pi/2$ pulse has also been superimposed at time zero to check M_0. Scale 0.5 sec/cm. (B) A T_2 measurement *via* the modified Carr–Purcell sequence. The spikes are anomalies caused by near-neighbor resonances. T_2 is the time constant for the exponential decay of the low humps between the spikes. Scale 1 sec/cm

monitoring $\pi/2$ pulses are seen to the right of the time zero pulses. Figure 3B shows the trace for a typical T_2 measurement on *the same* transition. These experiments used the well known[11] Carr–Purcell sequence[12] as modified by Meiboom and Gill.[13] Evaluation of these traces in the usual way gave the values for T_1 and T_2 shown in Table I.

Table I. Observed Values[a] of T_1 and T_2 (sec) for Transitions in the ^{1}H Nmr Spectra[b]

Transition no.	T_1	T_2	
	2-Bromo (**1**)		
1	1.9	1.9	H-1
2	1.8	1.8	H-1
3	1.9	1.7	H-3
6	1.8	1.5	H-3
7	1.4	1.2	H-4
10	1.4	1.2	H-4
Acetone		15.2	
	2-Chloro (**3**)		
1	2.0	1.8	H-1
2	1.9	1.8	H-1
3	2.0	2.2	H-3
8–9	1.3	1.1	H-4
10	1.2	1.2	H-4
Acetone		15.8	

[a] These values were obtained in deuteriobenzene solution containing TMS and acetone. The experimental error is at least ±10%. [b] The spectrum for **1** is given in Figure 1 and the transition numbering is indicated; that for the chloro analog **3** is closely similar.

Similar experiments were performed on the outer transitions 3, 6 and 7, 10 of the H-3 and H-4 quartets; apart from a small amount of interference from neighboring lines, these experiments caused no difficulty and the resultant relaxation times are listed in the table. However, it proved impossible to make any measurements with the "inner" components 4, 5 and 8, 9 because of the near degeneracy of these transitions. This was not unexpected; the two transitions were too close together for them to be examined separately and the use of a pulse sufficiently strong to perturb both transitions equally would violate the selectivity requirements and hence perturb[6] the outer transitions. More disappointing was the fact that it was not possible to make any satisfactory measurements of any of the remaining resonances; even the transitions of the H-6 quartet (11–14) were too close together for satisfactory traces to be recorded.

Experiments with the 2-chloro derivative (**3**) followed directly those described above; the measurements were confined to the H-1, H-3, and H-4 resonances to give the data listed in the table. In order that a direct comparison could be made between the data for these two derivatives, it was necessary that both solutions be as nearly identical as possible. A check on this point was made by measuring the T_2 relaxation time of a small quantity of acetone which had been added to each of the solutions prior to degassing. The values obtained were 15.2 sec for the solution of **1** and 15.8 for the solution of **3**; the difference between these values is well within the expected experimental error of ±10%.

The more dilute samples were then subject to T_1 experiments using a Fourier transform method.[7]

The spectra shown in Figure 4 illustrate quite clearly the power of this approach since the sequential decay of each of the resolved transitions is clearly observable. The T_1 values obtained *via* these Fourier transform experiments are summarized in Chart I.

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(11) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform N. M. R.," Academic Press, New York, N. Y., 1971.
(12) H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **94**, 630 (1954).
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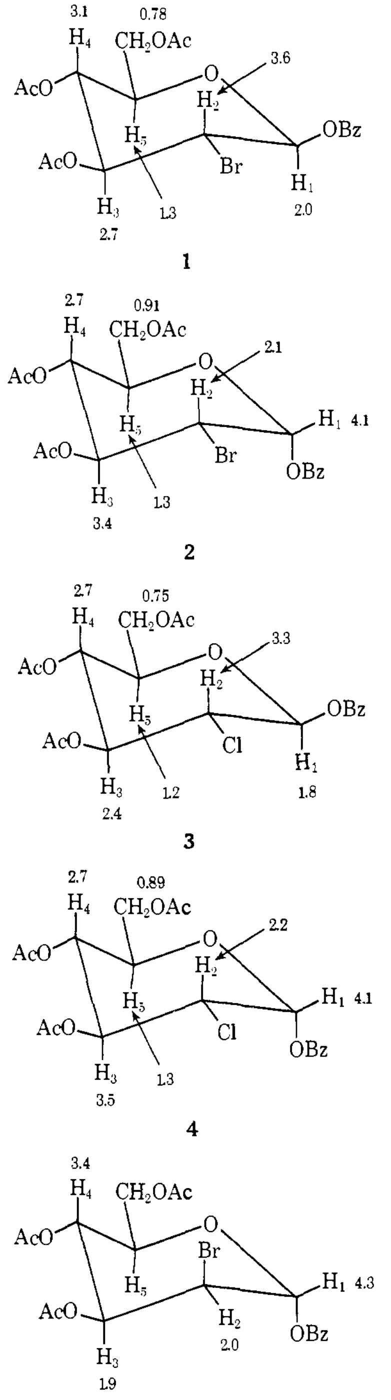
Chart I. Schematic Representation of the T_1 Values for the Assignable Protons of Derivatives **1–5**, as Measured by the Fourier Transform Method[a]



[a] The acetate methyl protons have T_1 values between 2.1 and 2.4 sec.

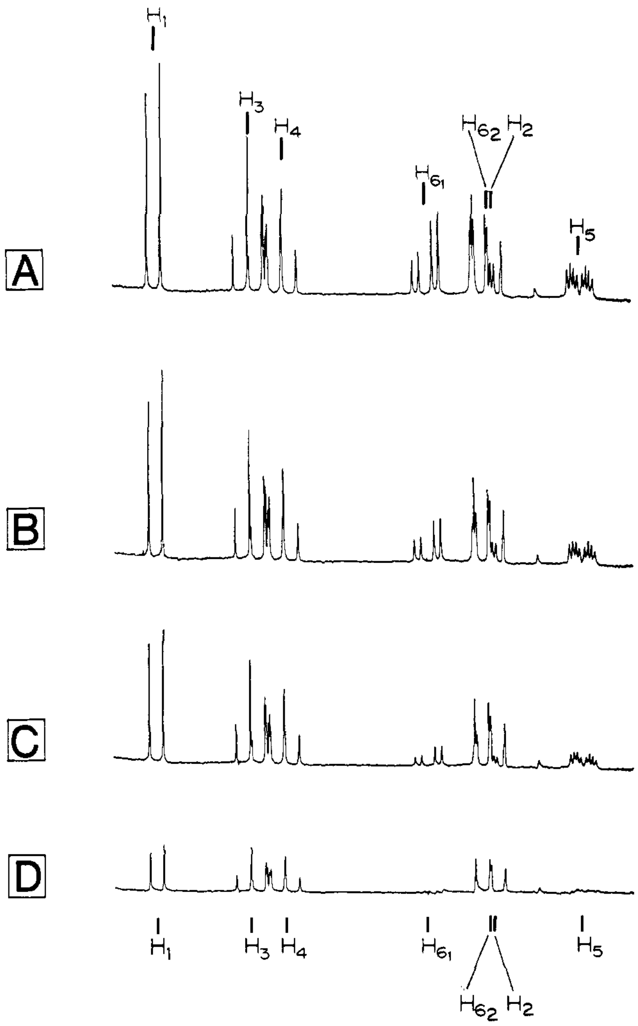


Figure 4. Partially relaxed ^1H nmr spectra (XL-100) for 3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-chloro-2-deoxy-β-D-glucopyranose (**3**) in benzene-d_6 solution. (A) The spectrum obtained with t = 0.1 sec; (B) with t = 0.5 sec; (C) with t = 1.0 sec; (D) with t = 3.0 sec. The overall intensity of all transitions decreases steadily through the series A → D. Note, however, that H-5, H-6_1, and H-6_2, which have the shorter relaxation times, have effectively decayed to zero intensity in D so that now the four transitions of H-2 are clearly resolved.

It should be noted that although there are some close agreements between T_1 values listed in Table I and in Figure 4, there are occasionally very sizable errors. These are most likely associated with the audiopulse method which is really being used beyond reasonable limits in certain of these experiments. Thus in the remainder of this discussion only the data obtained from the Fourier experiments will be used.

Several clearly discernible dependencies of these T_1 values deserve comment. First, the close similarity between the individual relaxation times of the configurationally identical pairs of compounds **1**, **3**, and **2**, **4** shows that the C-2 halogen substituents do not contribute appreciably to the proton relaxation. Second, the increase in the T_1 value of H-1 in going from the axial orientation (as in **1** and **3**) to the equatorial orientation (as in **2** and **4**) implies a marked configurational dependence for T_1 values. It is tempting to speculate that this dependence reflects the shorter distance, and hence the stronger dipole–dipole relaxation, between H-3a, H-5a, and H-1a, compared with that between the former protons and H-1e. Supporting evidence for this suggestion comes from the increase in T_1 values of the H-3a resonances, from 2.4 to 3.5 sec, that accompanies the removal of the H-3a and H-1a interaction (compare **1** with **2** and **3** with **4**). The same holds true for the H-4 resonances of the α-bromo benzoates **2** and **5** where inversion of the bromine at C-2 from the equatorial orientation (as in **2**) to the axial orientation (as in **5**) causes an increase in the T_1 value of H-4.

Intercomparison of the T_1 values also shows the

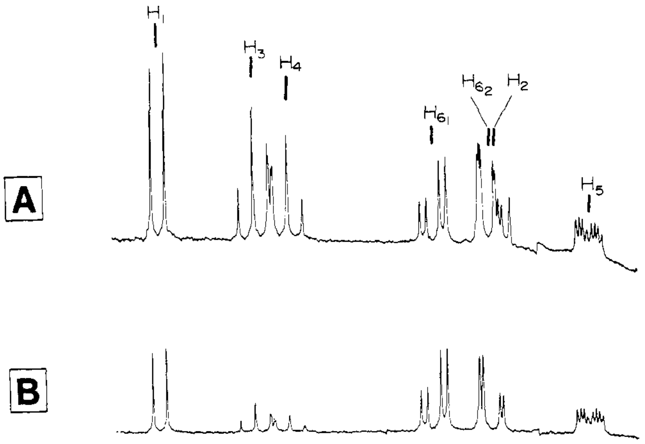


Figure 5. Partial 100-MHz spectra (XL-100) of **3** in benzene-d_6 solution. (A) The normal spectrum. (B) The partially relaxed spectrum determined with a 180°–t–90° sequence.

contributions that vicinal protons have on the relaxation. Compare for example the T_1 values of the H-2 resonances of the β, α pairs **1**, **2** and **3**, **4**. In both instances the change from a diaxial interaction to gauche interaction results in a substantial (*ca.* twofold) reduction in T_1. A similar dependence is found for the H-3 resonance of **2** and **5** where the gauche interaction of H-3 and H-2 of **5** reduces the T_1 values from 3.4 to 1.9 sec. Again, this distance dependence strongly implies the dominance of dipole–dipole interactions.

Further comparisons support these general trends, although some minor numerical inconsistencies serve to warn against any overly ambitious, simplistic rationales. Furthermore, it is clear that some circumstances can easily arise that can cause confusion. For example, the introduction of a gauche interaction between H-2 and H-3 as in going from **2** to **5** causes a very much smaller change in the relaxation time of H-2 than it does for H-3. Evidently here the introduction of the gauche (H-2 to H-3) interaction closely compensates for the loss of the 1,3-diaxial (H-2 to H-4) interaction.

One additional point which it seems relevant to make at this juncture is that the Fourier transform experiment used here constitutes a very effective method for facilitating assignments of ^{1}H nmr spectra of complex organic molecules. This point is rather nicely illustrated by the spectra shown in Figure 4. In the normal spectrum of **3** the transitions of H-2 overlap with those of the H-6$_2$ resonances. Because of the *ca.* twofold differential between the T_1 values of H-2 and H-6$_2$, it is possible to arrange a delay time such that the H-6$_2$ transitions have effectively decayed to zero intensity while the transitions of H-2 have decreased in intensity by *ca.* 75%.

Thus the three-pulse sequence, 180°–t–90°. . .90°, provides a useful method for detecting the most slowly relaxing resonance of an overlapping set. Observation of the most rapidly relaxing resonances is best accomplished by a two-pulse sequence, 180°–τ–90°, and this is illustrated in Figure 5.

Experience with other molecules suggest that whenever two protons have T_1 values differing by a factor of at least 2 or 3, or more, it is easy to detect separately the transitions of either proton. In view of the success of partially relaxed measurements for the assignment of carbon-13 spectra,[7c,8] we are surprised that other laboratories have not used this potential for proton studies.

Conclusions

The data presented in this paper clearly demonstrate several stereospecific dependencies for the longitudinal relaxation times of protons attached to a six-membered ring system. For an axially oriented proton, interactions between protons having either vicinal–gauche or 1,3-diaxial orientations make significant contributions to nuclear relaxation. For an equatorially oriented proton, only vicinal–gauche interactions are significant. Although attention has been directed here to carbohydrate systems, the dependencies appear to be quite general to other cyclic organic compounds and it seems probable that proton T_1 measurements will further extend the already considerable utility of proton nmr spectroscopy as a structural tool.

It is appropriate at this juncture to point out that, although the numerical values of the T_1 values that we have reported here are experimentally sound, it is extremely difficult to proffer any precise mechanistic description of their individual source. Indeed, in view of the many possible relaxation pathways that are available, it is quite remarkable that the stereospecific nature of the dependencies is as clear-cut as it is. However, this precise stereospecificity strongly implies that the dominant relaxation pathways involve dipole–dipole interactions which are known to be proportional to the inverse sixth power of the internuclear separation. Contributions from other relaxation mechanisms appear to be both small and systematic; for example, the near identity of the T_1 values of specific protons of **1** and **3** and of **2** and **4** suggests that each pair of molecules must be tumbling in solution with closely similar correlation times. However, in this regard it should be recognized that rotation about the C-5 to C-6 bond provides an extra degree of freedom for the protons attached to C-6 that could influence their relaxation times.

From a mechanistic standpoint, each of the experimentally determined relaxation times is a composite value containing contributions from many different sources. By working in reasonably dilute, degassed solutions in magnetically inert solvents, it is likely that the principal source of relaxation is the intramolecular dipole–dipole mechanism. However, because the nuclei that we have been studying are all part of a spin system that is closely coupled by scalar interactions, cross relaxation can be expected[14] to contribute toward the overall relaxation picture and preclude the possibility of simplistic rationales. In this respect, it is noteworthy that the data obtained for these derivatives contained none of the characteristic trends associated with cross relaxation; thus, the apparent T_1 values for each of the components of a multiplet resonance were identical within experimental error, and furthermore

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[14] I. Solomon, *Phys. Rev.*, **99**, 559 (1955); I. Solomon and N. Bloembergen, *J. Chem. Phys.*, **25**, 261 (1956); H. Shimizu and S. Fujiwara, *ibid.*, **34**, 1501 (1961); E. L. Mackor and C. Maclean, *ibid.*, **42**, 4254 (1965); J. H. Noggle, *ibid.*, **43**, 3304 (1965); E. L. Mackor and C. Maclean, *ibid.*, **44**, 64 (1966); R. A. Hoffman and S. Forsen, *ibid.*, **45**, 2049 (1966); C. Maclean, E. L. Mackor, and C. W. Hilbers, *ibid.*, **46**, 3393 (1967); R. Freeman, S. Wittekoek, and R. R. Ernst, *ibid.*, **52**, 1529 (1970); I. D. Campbell and R. Freeman, private communication.

the plots of "ln (peak height)" *vs.* "*t*" were linear and showed no evidence for nonexponential decay. In general, it is likely that cross relaxation may present a more formidable problem that it has for these derivatives.

Acknowledgments. This work was supported by the National Research Council of Canada (operating grants, A 1905, and equipment grants, E 1338 and E 1854) and by the Committee for Research at the University of British Columbia. It is a pleasure to thank Roland Burton of this Department for help with the construction of the audiopulse spectrometer and Dr. Ray Freeman of Varian Associates for helpful discussions.

A Theory Regarding the Role of Lone-Pair Interactions in "Through-Space" Fluorine–Fluorine Nuclear Spin–Spin Coupling

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Contribution from the Department of Chemistry, Bryn Mawr College, Bryn Mawr, Pennsylvania 19010. *Received June 22, 1973*

Abstract: A theoretical description of the mechanism of "through-space" fluorine–fluorine nuclear spin–spin coupling is presented, based on the concept that two lone-pair orbitals from spatially proximate fluorines can interact by direct overlap to form one bonding and one antibonding molecular orbital delocalized over both fluorines. Positive coupling constants are explained in terms of spin-correlation effects (Hund's rule behavior) of the electrons in these two-center molecular orbitals and Fermi contact interactions of the spin-polarized fluorine core electrons. The pronounced dependence of the magnitude of this type of coupling on the distance between the two fluorines is accounted for in terms of the Pauli exclusion principle and the extent to which the bonding and antibonding orbitals differ in their electron density distributions.

The existence of a "through-space" mode of spin–spin coupling between two fluorine nuclei[1] has been convincingly demonstrated by a number of observations of large-magnitude coupling constants in molecules in which the two coupled fluorines are in close spatial proximity (*i.e.*, an F–F distance of about 2.7 Å or less) but are separated by four or more bonds.[2] The cases known thus far involve molecules of three different structural types, **1**–**3**; some examples are indicated in Figure 1.

1

2

3

There are two key characteristics of this type of coupling: the magnitude of the coupling constant depends strikingly on the distance of separation of the two fluorine nuclei, as has been shown most clearly by the recent studies of Servis and Jerome;[2n,t] and the sign of the coupling constant has been found to be positive in each of the 17 reported cases in which the appropriate double or triple resonance experiments have been carried out.[2i,m,r,v]

It is the purpose of this paper to present a detailed, qualitative, theoretical formulation to explain the mechanism of "through-space" coupling between fluorine nuclei. Such an explanation has apparently not been given previously, although it has often been suggested in various ways that the overlap of a pair of 2p lone-pair orbitals at distances less than twice the van der Waals radius of fluorine or the contribution of resonance structures with a "long bond" between the fluorines is somehow involved.[1,2b,d,h,i,m,3–6]

Of the many attempts to develop quantum mechanical theories to serve as a basis for quantitatively

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