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No. 15

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The orientation of substitution reactions in trimeric phosphonitrilic chloride.

From the aminolysis of trimeric phosphonitrilic chloride (I) with dimethylamine the products $P_3N_3R_nCl_{6-n}$ have been obtained, where $R = (CH_3)_2N-$ and $n = 1, 2, 3, 4$ and 6 . The orientations of the dimethylamino groups in these compounds have been determined from their proton magnetic resonance spectra.

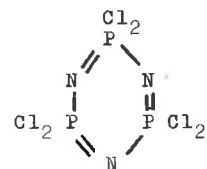
The spectrum of the mono-substituted compound consists of a 1:1:1 triplet centred at 2.1 ppm (external water reference) while the hexa-substituted compound shows a similar triplet centred at 2.3 ppm. These shifts are taken as characteristic of the protons in the dimethylamino groups in the environments (II) and (III).

The spectra of the bis- and tris-substituted compounds consist of a triplet centred at 2.1 ppm while the tetra-substituted compound has a spectrum consisting of two triplets of approximately equal areas centred at 2.0 and 2.3 ppm. These results indicate that the structures of the bis-, tris and tetra-substituted compounds are as shown in (IV) - (VI).

In the case of this reaction substitution proceeds by the replacement of single chlorine atoms at each phosphorus, and only after the formation of the symmetrical tris-dimethylamino triphosphonitrilic chloride are compounds containing structure (III) produced.

Thanks are due to Dr. R. Shaw of Birkbeck College for providing samples of substituted phosphonitrilic compounds.

R. White,
University College,
London.



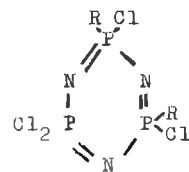
(I)



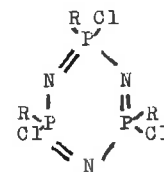
(II)



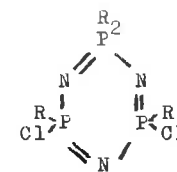
(III)



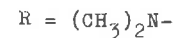
(IV)



(V)



(VI)



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UNION CARBIDE RESEARCH INSTITUTE

December 15, 1959

Dr. A. A. Bothner-By
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Dear Dr. Bothner-By:

Thank you for adding my name to your MELLON-M-R mailing list and supplying me with a set of back issues. In order to be a paying subscriber, I have included a table I have found very handy in analyzing spectra of the ABX_N type where the X group is completely reducible by group operations and is perturbed only to first-order by the AB system. It applies equally well to ABX_2 , and ABX_3 types where all nuclei are of spin 1/2. Eigenstates are designated according to their group representation, Γ , and the s components of total spin for the AB group (superscript to left) and X_N group (subscript to right). M refers to the N+1 eigenvalues of the latter, ω to the shift in cps from a convenient reference for the nucleus subscripted, and the remaining parameters are apparent either from the table or from common usage.

In applying the table to cases, it is convenient to specify the A and B protons according to $|J_{AX}| > |J_{BX}|$ and to arbitrarily assign positive signs to the indeterminate couplings J_{AX} and J_{AB} . We are then assured that $J_{AX} \pm J_{BX} > 0$ but cannot specify the signs of either J_{BX} or $\Delta\omega = \omega_A - \omega_B$. It is then noted that the X group spectrum is completely symmetrical about ω_X , fixing this parameter, and that the two lines in this group split by $J_{AX} + J_{BX}$ are the most intense in the set (unless no AB mixing occurs, whereupon the analysis may proceed by first-order splittings throughout), fixing this sum.

There will be remaining in this group 2N lines on each side of ω_X which can be divided on the basis of intensities into two subgroups of N each. The splittings of the stronger set with their counterparts across ω_X give N equations in the N+1 constants, C_M , having the forms $\Delta\nu = \sum (C_{M+1} - C_M)$. Another N equations of the form $\Delta\nu = C_{M+1} + C_M$ are available from the weak set provided their intensities are observable. It is hence often possible to determine all the C_M 's, and from them the quantities $J_{AX}-J_{BX}$, J_{AB} , and $|\Delta\omega|$ using equations of the form:

$$(2C_M)^2 = \Delta\omega^2 + 2M\Delta\omega\Delta J + M^2\Delta J^2 + J_{AB}^2$$

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$$(2C_{M+1})^2 - (2C_M)^2 = 2\Delta\omega\Delta J + (2M+1)\Delta J^2 \quad (\Delta J = J_{AX} - J_{BX})$$

This virtually solves the problem, and the sign of $\Delta\omega$ as well as a check on the other assignments is available from the AB lines.

In case the X group lines are not well enough resolved to allow an accurate approach by this method, we can attack instead the AB group by noting it consists of N+1 quartets each resembling a two-spin problem, and that the centers of gravity of these quartets are evenly spaced by $1/2(J_{AX}+J_{BX})$, or one-half the splitting of the most intense X group lines. I find a sliding scale marked off in units of $1/2(J_{AX}+J_{BX})$ convenient in picking out these quartets, after which the analysis is straightforward. All four lines of every quartet may not be observable, of course, but when the outer lines are weak the inner nearly coincide.

While at Emory I had occasion to apply this table to a considerable number of spectra of both ABX_2 and ABX_3 types, finding it quite handy for both. We have worked out some general forms for the slightly perturbed (i.e., second-order) cases, as well, but these are not as simple to summarize or apply.

Sincerely yours,

E. B. Whipple

EBW:bg
Encl. 1

ABX_N Spectrum

Transition	Frequency	Intensity
${}^1(\Gamma)_M - {}^0(\Gamma)_M$	$\frac{1}{2}(\omega_A + \omega_B) + \frac{1}{2}J_{AB} + \frac{1}{2}M(J_{AX} + J_{BX}) \mp C_M$	$\frac{1}{2}I_M (1 \pm \sin 2\theta_M)$
${}^0(\Gamma)_M - {}^{-1}(\Gamma)_M$	$\frac{1}{2}(\omega_A + \omega_B) - \frac{1}{2}J_{AB} + \frac{1}{2}M(J_{AX} + J_{BX}) \pm C_M$	$\frac{1}{2}I_M (1 \mp \sin 2\theta_M)$
${}^1(\Gamma)_{M+1} - {}^1(\Gamma)_M$	$\omega_X + \frac{1}{2}(J_{AX} + J_{BX})$	$2^{N-1} I_M$
${}^{-1}(\Gamma)_{M+1} - {}^{-1}(\Gamma)_M$	$\omega_X - \frac{1}{2}(J_{AX} + J_{BX})$	$2^{N-1} I_M$
${}^0(\Gamma)_{M+1} - {}^0(\Gamma)_M$	$\omega_X \pm (C_{M+1} - C_M)$	$\frac{1}{2}I_M \left(\frac{1}{2}N+M\right) \left(\cos\theta_{M+1} \cos\theta_M + \sin\theta_{M+1} \sin\theta_M\right)^2$
	$\omega_X \pm (C_{M+1} + C_M)$	$\frac{1}{2}I_M \left(\frac{1}{2}N+M\right) \left(\cos\theta_{M+1} \sin\theta_M - \sin\theta_{M+1} \cos\theta_M\right)^2$

$$2C_M = \sqrt{\left[(\omega_A - \omega_B) + M(J_{AX} - J_{BX})\right]^2 + J_{AB}^2}$$

$$2C_M \sin 2\theta_M = J_{AB}$$

$$\frac{1}{2}I_M = \frac{N!}{\left(\frac{1}{2}N+M\right)! \left(\frac{1}{2}N-M\right)!}$$

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NS/VMR.

Drs. A.A. Bothner-By and
B.L. Shapiro,
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U.S.A.

16th December, 1959.

Dear Aksel and Barry,

I am very sorry that you should have had to prod me to write a contribution to MelloN-M-R. I have had it in mind since I returned from my visit to the U.S.A. this summer, but somehow it didn't get written. However, let me say how very much all the NMR group here enjoy and appreciate the News letter.

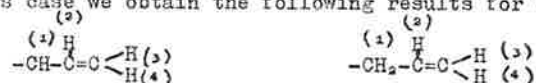
We have been continuing our efforts to unravel certain features of the NMR spectra of hydrocarbon groupings. For example, we have recently used the ¹³CH satellite technique^(1,2) to obtain what we think is an accurate analysis of the complex spectrum of propane as observed at 40 Mc. About 2% of propane molecules have the formula ¹³CH₂-¹²CH₂-¹³CH₃ and the methyl groups of these give rise to widely separated ¹³CH triplet sidebands (J_{13CH₂} ~ 124 c/s) of which the one at high field to the main CH₂ resonance is not difficult to observe and measure. The spacing of this triplet is 13.66 ± 0.20 c/s, and allowing (by calculations on simpler model systems using a digital computer) for perturbing effects caused by the presence of the ¹²CH₂ protons at the other end of the molecule, we deduce that J(CH₂-CH₂) is ~ 7.5 c/s. With this information it was a fairly simple matter (again given the computer) to find an accurate analysis of the spectrum with J = 7.4 c/s and J(CH₂-CH₃) = 17.5 c/s. These values may be compared with earlier ones deduced directly from 40 Mc and 60 Mc spectra without the use of the ¹³CH sidebands.⁽³⁾

Following an earlier work by Alexander⁽⁴⁾ on 3,3-dimethyl butene-1 and butene-1 we have made a detailed analysis of the vinyl part of the spectrum of ¹³C(CH₃)₂-CH=CH₂ molecule as an

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XABC problem. As you know, from XABC spectra one can in principle obtain the relative signs of all coupling constants. In this case we obtain the following results for comparison



with those of Alexander on butene-1

<u>3-methyl-butene-1</u>	<u>butene-1 (Alexander)</u>
J_{24} 17.3 *	17.4 *
J_{23} +10.4	+10.4
J_{34} +1.6	+1.9
J_{12} +6.5	±6.3
J_{13} -1.2	} 1.9 } ± and 1.3
J_{14} -1.7	

* assumed to be positive - other signs are relative to this.

It is seen that the results for the two molecules are remarkably close, but that we have been able to resolve the uncertainty about the signs of J_{12} and J_{13}, J_{14} with respect to the coupling constants of the vinyl group. Both Mortimer⁽⁵⁾ and ourselves⁽⁶⁾ have recently drawn analogous conclusions from analyses of the spectra of chlorinated propenes, but we thought that it would be a good thing to check on another hydrocarbon. It seems that only the long-range coupling constants J_{13} and J_{14} are of opposite sign to the remainder in these hydrocarbons. Karplus' excellent calculations⁽⁷⁾ on the coupling constants of cis and trans olefinic CH=CH groups, suggest that the sign we have assumed for the trans coupling constants is the correct one; if so the other signs are also correct.

Finally I would like to give a preliminary report on some measurements that we have been making on the H-H coupling constants of SiH₂ groups in SiH₂I₂, SiH₃I, and SiH₄ using

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deuterium substitution. The approximate values that we obtain for the magnitudes of these constants are 22.7, 11.7 and <1.5 c/s respectively. They show a remarkable variation which is apparently in the opposite direction to that observed on going from CH₂Cl₂ (7.1) to CH₄ (12.4 c/s),⁽⁶⁾ of course the variation would really be in the same direction, if in fact the coupling constants are of the opposite sign, i.e., if the SiH₂ constants are negative (assuming the CH₂ constants to be positive as deduced theoretically by Karplus and Anderson)⁽⁹⁾ If I understood correctly a conversation I had with Martin Karplus during the summer, it is more likely that the SiH₂ constants should be negative, because the greater H-H distances makes positive contributions to the coupling constants from direct H-H bonding (and electron pairing) less than in the CH₂ case.

Yours sincerely,

Norman

Norman Sheppard.

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