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Proton Resonance Spectra of Thiopyrones

by

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PROTON RESONANCE SPECTRA OF THIOPYRONES

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The proton magnetic resonance spectra of 4-pyrone, 4-thiapyrone, 4-thiopyrone, and 4-thiothiapyrone have been observed and analyzed. Comparisons of the experimental spectra with those calculated for all combinations of relative signs for the coupling constants indicate that in each molecule the coupling constants have the same sign, which presumably is positive. The average deviation between the observed line positions and those calculated for each of the various sign permutations is found to be a useful criterion in assigning the relative signs. The effect on the coupling constants of the introduction of sulfur into the molecule is discussed. The downfield shift of the midpoint of the spectra, found upon sulfur introduction, is interpreted in terms of an increased ring current.

Introduction

As an aid in developing an adequate theory of the proton-proton couplings in heterocyclic unsaturated molecules, more experimental data on the n.m.r. spectra of these systems are desirable. In this context, the thiopyrones studied in the present paper are interesting for several reasons. The spectra of these compounds are of the A_2B_2 type and amenable to a rigorous analysis. Furthermore these compounds form a series of closely related molecules suitable for a study of the effect upon n.m.r. spectral parameters of the replacement of oxygen by sulfur. Another feature is the presence of oxygen or sulfur in the ring, which may provide information on the transmission of proton-proton coupling through an heteroatom. The polarographic behavior and chemical reactivity[1] of the thiopyrones have recently been studied as have

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(1) C. Parkányi and R. Zahradník, Collection Czech. Chem. Commun. 27, 1355 (1962).

the physical properties,[2] and quantum chemical calculations have been made,[2] and hence there is also interest in their n.m.r. parameters.

The general analysis of A_2B_2 type spectra has been discussed by a number of authors[3-6] who treated the effects of the magnitudes and relative signs of the n.m.r. parameters on the spectra in considerable detail. In the present paper the n.m.r. spectra of 4-pyrone, 4-thiapyrone, 4-thiopyrone, and 4-thiothiapyrone have been analyzed and their chemical shifts and coupling constants are compared. Optimum values of the latter were calculated for all combinations of signs of coupling constants for each compound, and the calculated spectra were compared with the experimental ones. In the case of the strongly coupled 4-thiothiapyrone, the comparison showed unambigously that all four coupling constants have the same sign; in the less strongly coupled 4-thiapyrone, and 4-thiopyrone cases this is the most probable assignment. But for the weakly coupled 4-pyrone, an assignment could not be made on this basis as the calculated spectra are almost independent of the combination of signs used, and the choice of all having the same sign is made by analogy with the other three compounds.

Experimental Procedure and Results

The n.m.r. spectra were recorded with a Varian A60 spectrometer. The spectrum of each compound was run 8 times and the arithmetic mean of each line

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(2) R. Zahradník, C. Parkányi, and J. Koutecký, Collection Czech. Chem. Commun. 27, 1242 (1962).

(3) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, 1959.

(4) B. Dischler, and G. Englert, Z Naturforsch. 16a, 1180 (1961).

(5) D. M. Grant, R. C. Hirst, and H. S. Gutowsky, J. Chem. Phys. 38, 470 (1963).

(6) H. M. Hutton and T. Schaefer, Can. J. Chem. 41, 2429 (1963).

position is used. The standard deviation in the mean line positions is ±0.08 cps, except when several lines overlap. The spectrometer resolution was 0.4 cps, but in the spectra of 4-thiothiapyrone the line widths were 0.8 cps possibly due to traces of decomposition products.

The compounds, all crystalline solids, were measured as 0.15 mole fraction solutions in $CDCl_3$, and tetramethyl silane was added as an internal reference. The chemical shift between the A_2 and B_2 protons is concentration dependent. This dependence was studied in the neighborhood of 0.15 mole fraction. The change of chemical shift with dilution may be given as a quantity S defined as the change in magnitude of the chemical shift (in cps) per decrease in mole fraction of 0.01, calculated at 0.15 mole fraction. The values obtained for 4-pyrone, 4-thiapyrone, 4-thiopyrone, and 4-thiothiapyrone are S = 0.2, 0.3, 0.3 and -0.3, respectively. The relative positions of the lines observed in individual multiplets are practically independent of concentration in the 0.10 to 0.20 mole fraction range.

The samples of 4-pyrone, 4-thiapyrone, 4-thiopyrone, and 4-thiothiapyrone were provided by Dr. C. Parkányi of the Institute of Physical Chemistry of the Czechoslovak Academy of Science. Prague. The physical constants and synthesis of the thiopyrones are described in a recent paper by Parkányi and Zahradník.[1] The samples of 2,6-, and 3,5-dimethyl-4-pyrones[7,8] were supplied by Dr. P. Beak of this laboratory. The sample of 2,6-dimethyl-4-thiopyrone[9] was obtained from Dr. M.A.F. Elkaschef of the National Research Centre, Cairo, U.A.R.

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(7) P. Beak, Tetrahedron 20, 831 (1964).

(8) P. Beak and G. A. Carls. J. Org. Chem. 00,0000 (1964).

(9) Mohamed A.-F. Elkaschef and M. H. Nosseir. J. Chem. Soc. 4643 (1963).

The analyses of the A_2B_2 spectra were carried out using the Swalen-Reilly[10] iterative programs for analysis of complex n.m.r. spectra (NMREN 1, NMRIT) and were run on the University of Illinois IBM 7094 computer. The results of the analyses are given in Table I. The structural formulae of the compounds and the definitions used in designating the protons and coupling constants are shown in Fig. 1.

Discussion

A_2B_2 Spectra of Thiopyrones. The n.m.r. spectra of A_2X_2 and A_2B_2 spin systems have been discussed in detail in several papers.[3-6] Analysis of the spectra of the thiopyrones is straightforward so we will limit discussion of it to a minimum. An A_2B_2 spectrum, except in the case of very strong coupling, is composed of a highfield and a lowfield multiplet. But it is not possible to assign these multiplets to the A_2 and B_2 nuclei in the molecule without further information. Fortunately, methylated 4-pyrones and a methylated 4-thiopyrone were available and the chemical shifts of the ring protons of these compounds permitted assignments to be made for the thiopyrones by comparison. The chemical shift of the ring protons in 3,5-dimethyl-4-pyrone is 456 cps downfield from TMS at 60 Mc/s; in 2,6-dimethyl-4-pyrone, it is 361 cps; and in 2,6-dimethyl-4-thiopyrone, 416 cps. Upon comparing these values with those given in Table I for 4-pyrone (483 and 389 cps) and 4-thiopyrone (470 and 416 cps), we assign the lowfield multiplet to the protons in the 2 and 6 positions (A protons) and the highfield multiplet to those in the 3 and 5 positions (B protons) for both compounds. In the absence of further experimental data, we assume the same assignments to be valid for 4-thiapyrone, and 4-thiothiapyrone. Calculations of the electron density at the carbon atoms have been made using the MO LCAO

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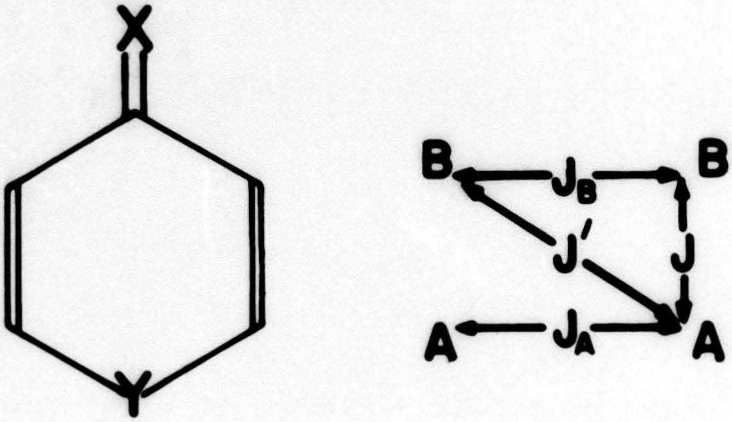
(10) J. D. Swalen and C. A. Reilly, J. Chem. Phys. 37, 21, (1962).

Table I: Chemical Shifts and Coupling Constants of Thiopyrones[a]

Compound	ν_A	ν_B	$\Delta\nu$	J_A	J_B	J	J'
4-Pyrone	482.6	389.3	93.3	2.8_9	1.2_2	6.3_3	0.4_2
4-Thiapyrone	469.5	415.7	53.8	4.1_2	2.0_0	10.7_4	0.4_4
4-Thiopyrone	448.6	421.9	26.7	2.2_0	0.8_8	5.7_8	0.6_5
4-Thiothiapyrone	471.8	452.5	19.3	3.4_1	1.7_9	10.3_9	0.6_7

[a] All values are in cps. The symbols used to designate the protons and coupling constants are defined in Fig. 1. The chemical shifts are in cps downfield from TMS at 60 Mc/s.



X = O, Y = O	4-Pyrone
X = O, Y = S	4-Thiapyrone
X = S, Y = O	4-Thiopyrone
X = S, Y = S	4-Thiothiapyrone

Fig. 1. The structural formulae of the thiopyrones, with the designations used for the protons and coupling constants.

approximation[2] for all of the thiopyrones studied here. The electron density was found to be higher at the 3 and 5 positions than at the 2 and 6, which is consistent with the high-field assignments of the former.

The general appearance of the thiopyrone spectra studied by us is the same; the main difference is the decrease in the chemical shift between the A_2 and B_2 protons in going from 4-pyrone to 4-thiothiapyrone. A schematic high-field multiplet of a general thiopyrone spectrum is shown in Fig. 2; the transitions are numbered as in previous work.[3,5] In all of the spectra, the lines due to transitions 3 and 4 overlap as do 1 and 2. This and similar overlap in the lowfield multiplet reduce the number of resolved lines from 24 to 20. In the spectra of 4-pyrone and 4-thiapyrone, lines 9 and 12 are observed as shoulders on intense neighboring lines but for 4-thiopyrone and 4-thiothiapyrone they were not resolved and the number of observed lines is reduced to 16.

Analyses of the spectra were performed for all combinations of relative signs for the coupling constants, by means of the Swalen-Reilly[10] energy level program MNREN 1 and the iterative program NMRIT. For each sign combination, the program converged to an optimum set of values for the parameters ν_a, ν_b, and the four coupling constants. The magnitudes obtained for a particular parameter depend upon the sign combination but the main differences are the changes in the signs themselves. Therefore, we give only the final assigned sets of values, which are in Table I. A measure of relatively how well the different sets of parameters agree with experiment is the average deviation between the positions of the observed lines and those calculated with each set of parameters. These average deviations are listed in Table II for the eight relative sign combinations for each compound. For 4-thiothiapyrone the best fit by a 3-fold factor is obtained when all the signs are the same. The results of the calculations for 4-thiopyrone favor sign assignments of ++++ and ++-- for J_A,

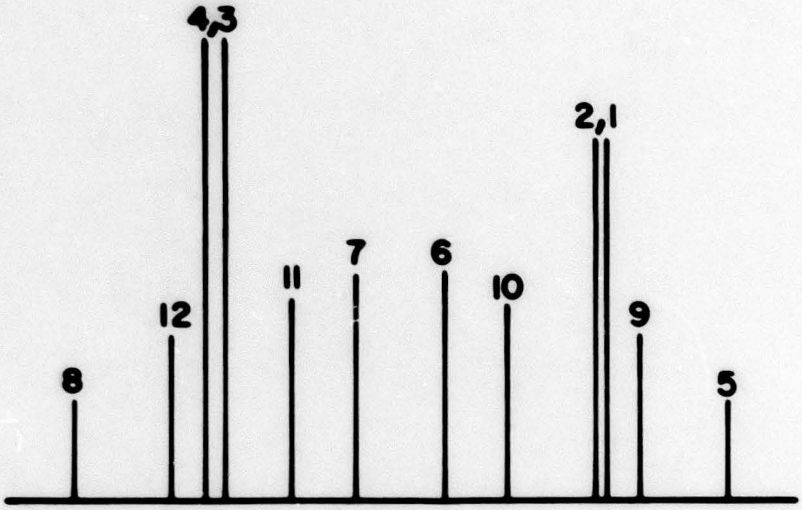


Fig. 2. Schematic appearance of the highfield multiplet of the thiopyrone spectra. The frequency and intensity scales are arbitrary. For numbering of the transitions, see reference 5.

Table II: Average Deviations in cps Between the Transition Frequencies[a] for the Best Fit Calculated and the Observed Spectra of Thiopyrones Obtained by NMRIT for Each Combination of Relative Signs of the Coupling Constants[b]

Compound	Average deviation for given combination of signs							
	++++	-+++	+-++	++-+	+++-	++--	+--+	+-+-
4-Pyrone	0.023	0.025	0.025	0.020	0.023	0.020	0.025	0.025
4-Thiapyrone	0.047	0.073	0.069	0.054	0.047	0.054	0.073	0.069
4-Thiopyrone	0.077	0.096	0.092	0.389	0.374	0.058	0.394	0.394
4-Thiothiapyrone	0.113	0.311	0.269	0.540	0.396	0.322	0.530	0.530

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[a] A similar analysis of the integrated intensities also can be used as an aid in establishing the correct combination of relative signs.

[b] The signs given correspond to the following order of the coupling constants: J_A, J_B, J, J'.

J_B, J and J' respectively. However, if the sign of J changes on going from 4-thiothiapyrone to 4-thiopyrone then, as may be seen in Table I, its magnitude changes by about 16 cps. This seems very unlikely, so the sign combination ++++ is assigned to 4-thiopyrone. Similar reasoning in the case of 4-thiapyrone eliminates the sign combinations +++-, ++-+, and ++-- which give nearly the same low average deviation as does the combination ++++.

The spectrum of 4-pyrone closely resembles an A_2X_2 spectrum, and it is almost insensitive to change in relative signs of the coupling constants, as can be seen from Table II. To illustrate how closely the spectrum of 4-pyrone resembles an A_2X_2 spectrum, the results of an A_2X_2 analysis for this compound are, in cps: $J_A = 2.88$, $J = 1.21$, $J = 6.36$, and $J' = 0.39$, all of which agree to within 0.03 cps of the values given in Table I for the A_2B_2 analysis. However, in view of the close similarities in the magnitudes of the coupling constants for 4-pyrone and the other three thiopyrones, we conclude that their relative signs are the same. Moreover, it seems most probable that these signs are positive. The finding that the coupling constants are of the same sign in the thiopyrones agrees with previous results on the signs of the coupling constants in aromatic and other heteroaromatic systems.[11-16]

<u>Effect of Replacement of Oxygen by Sulfur on N.M.R. Parameters.</u> A comparison of the values for ν_A and ν_B in Table I shows that the chemical shift $\Delta\nu$ between

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(11) H. S. Gutowsky, C. H. Holm, A. Saika, and G. A. Williams, J. Am. Chem. Soc. 79, 4596 (1957).

(12) R. E. Richards and T. Schaefer, Mol. Phys. 1, 331 (1958).

(13) R. E. Richards and T. Schaefer, Trans. Faraday Soc. 54, 1280 (1958).

(14) B.D.N. Rao and J. D. Baldeschwieler, J. Chem. Phys. 37, 2473 (1962).

(15) W. G. Patterson and G. Bigam, Can. J. Chem. 41, 1841 (1963).

(16) R. Freeman, N. S. Bhacca, and C. A. Reilly, J. Chem. Phys. 38, 293 (1963).

the A_2 (2,6) and B_2 (3,5) protons is reduced as sulfur is introduced into the molecule. This reduction may be ascribed to the smaller electronegativity difference between C and S compared to that between C and O. In addition to the decrease in $\Delta\nu$, there is a concurrent downfield displacement of the average chemical shift $(\nu_A+\nu_B)/2$. One would expect the decreased electronegativity difference to produce upfield shifts,[3] so some other effect must be present. The average chemical shifts for the thiopyrones and some similar compounds[17] are listed in Table III, and in all heterocyclic "aromatic" compounds the shift of the sulfur derivative is downfield from that of the oxygen. It is apparent that this downfield shift is not the result of diamagnetic anisotropy of the sulfur because both cyclic and acyclic saturated compounds have an upfield shift, as expected from the electronegativity difference. The fact that only the unsaturated heterocyclic compounds have the downfield shift leads us to propose that it occurs as a result of an increased ring current in these compounds. Elvidge and Jackman[18] have based their definition of aromatic character on the ability of a compound to sustain an induced ring current. Therefore, in these terms the aromatic character and the delocalization of pi-electrons increase when going from 4-pyrone to 4-thiothiapyrone. This observation may be regarded as evidence that due to its d orbitals sulfur exhibits greater ability to enter into conjugation than oxygen.[19]

It is also interesting to compare the magnitudes of the coupling constants obtained by analyzing the spectra observed for the four thiopyrones. As is well known, the analysis of an A_2B_2 spin system does not distinguish between J_A and

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(17) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, 1959.

(18) J. A. Elvidge and L. M. Jackman, J. Chem. Soc. 859 (1961).

(19) H. C. Longuett-Higgins, Trans. Faraday Soc. 45, 173 (1949).

Table III: Average Chemical Shifts of the A_2 and B_2 Protons in Thiopyrones and Related Compounds

Compound	Chemical shift[a]	Compound	Chemical shift
4-Pyrone	435 cps	Thiophene[b]	432 cps
4-Thiopyrone	435	Tetrahydrofuran[b]	168
4-Thiapyrone	443	Tetrahydrothiophene[b]	142
4-Thiothiapyrone	462	Anisole[b]	227
Furan[b]	414	Thioanisole[b]	148

[a] The shifts, at 60 Mc/sec, are downfield from TMS and correspond to the midpoint of the A_2B_2 spectrum.

[b] Data taken from reference 17.

J_B, nor between J and J'. However, by means of other information, a tentative assignment can be made of the J_A coupling constant to coupling between the 2,6 protons (AA in Fig. 1) and of J_B to coupling between 3,5 protons. This is based on the following facts. It has been found[20] for furan and thiophene that sulfur substitution increases J (our J_A) from 1.55 to 2.85 cps. Similarly, recent data[21] on oxazole and thiazole derivatives have shown that J (J_A) in 4-methyloxazole is 1.0 cps whereas in 4-methylthiazole this coupling constant is 1.86 cps. Thus, we would expect an increase in J_A of 0.9 to 1.3 cps to accompany the replacement of the endo-oxygen by sulfur in the thiopyrones.

Fortunately, the values found for J_A and J_B are such that there is only the one way, given in Table I, of arranging the coupling constants so that replacement of the endo oxygen by sulfur causes an increase of ~1 cps, i.e., upon going from 4-pyrone to 4-thiapyrone and from 4-thiopyrone to 4-thiathiopyrone. Moreover, this increase is 1.2 cps for what we list as J_A and appreciably less, 0.8 cps, for J_B. Because of this difference we tentatively assign J_A as the coupling between the 2,6 protons which thus ranges from 2.2 to 4.1 cps and J_B, the 3,5 coupling from 0.9 to 2.0 cps.

The assignment of the coupling constants J and J' can be made without ambiguity. For each of the four compounds, one of these constants is large (5.8 to 10.7 cps) and the other small (0.4 to 0.7 cps). The large constant is assigned as J, the coupling between the ortho protons 2 and 3 (5,6), and the small is assigned as J', the cross coupling constant between para protons 2 and 5 (3,6). The assignment is made by comparison with ortho and para coupling constants in aromatic systems.[11]

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(20) R. J. Abraham and H. J. Bernstein, Can. J. Chem. 39, 905 (1961).

(21) P. Haake and W. B. Miller, J. Am. Chem. Soc. 85, 4044 (1963).

A distinct change in the value of the J coupling constant accompanies the introduction of sulfur into the ring, as can be observed in Table I. This coupling constant changes from approximately 6 cps in 4-pyrone and 4-thiopyrone to 10 cps in 4-thiapyrone and 4-thiothiapyrone. A similar change of the corresponding coupling constant is observed between furan and thiophene (the coupling constant increases from 1.8 cps to 4.7 cps). In the latter case Abraham and Bernstein[20] ascribed the change to the decrease in the CCH bond angles produced by introducing a larger sulfur atom into the five-membered ring. Also, there is a large amount of evidence that the vinyl coupling constant increases with the ring size in cyclic olefins.[22] However, it has been argued[23] that the change of J in thiophene compared to furan is primarily an electronegativity effect upon the ionic character of the C-H bonds which are alpha to the endo oxygen or sulfur. It seems reasonable to assume that both these effects operate in the thiopyrones and tend to increase the J coupling constant upon substitution of sulfur for oxygen in the ring.

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(22) O. L. Chapman, J. Am. Chem. Soc. 85, 2014 (1963).

(23) H. S. Gutowsky and A. L. Porte, J. Chem. Phys. 35, 839 (1961).

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