Pergamon

Tetrahedron, Vol. 53, No. 29, pp. 10113-10122, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00352-9

^{1}H and ^{13}C NMR of Some α-Halo Derivatives of *o*-Xylene

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Abstract: ^{13}C and ^{1}H NMR data for a series of α-halo derivatives of *o*-xylene are presented. A dynamic ^{1}H NMR investigation of α,α,α',α'-tetrabromo-*o*-xylene (**5**) was performed and the spectrum of the most stable conformer at 213 K is presented. The free energy of activation for the rotation of the $CHBr_2$ groups in **5** are determined for the first time. © 1997 Elsevier Science Ltd.

The continued interest in benzyl halides and related molecules finds its source in the flexibility these precursors have been shown to possess,[1] permitting one to obtain free-radicals, cations, quinodimethanes and even carbenes (from benzal halides), depending on the experimental conditions employed. Light-initiated radical cyclizations and polymerizations are examples of the applications of benzyl (and/or benzal) halides in photochemical synthesis,[1] while their most recent involvement (potential or actual) in industrial processes includes the photogeneration of hydrohalogenic acids (of paramount importance for the production of higher density microchips) and their use as precursors to electrical-conducting polymers,[2] generated by electrochemical means.

However, it was surprising to verify, in the course of our studies[3] on the photochemistry and photophysics of the title compounds, that data regarding the iodinated and higher brominated side-chain derivatives are at best scanty.

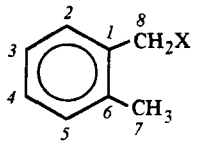
Hence, in the present paper we report our own NMR data from a series of halo derivatives of *o*-xylene (**Fig. 1**), including some compounds (**1a**, **2a** and **5**) which spectra had been previously published[4-7] to contribute to a better view of the self-consistency of the whole dataset. Moreover, in the case of the ^{13}C data we have also included literature data[5] on *o*-xylene itself and some of its chloro derivatives, for the sake of completeness.

We also present a ^{1}H DNMR study of α,α,α',α'-tetrabromo-*o*-xylene (**5**) from which we were able to determine the free energy of activation for the rotation of the $CHBr_2$ groups in compound **5**, whose spectra show temperature dependence features attributable to a surprisingly high side-chain rotational barrier.

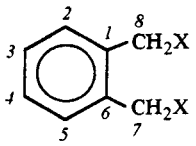
RESULTS AND DISCUSSION

The ^{1}H NMR chemical shifts (δ) of these *o*-xylene derivatives are presented in Table 1. The shifts corresponding to the side-chain protons, in good agreement with the data available in literature,[4,7] were assigned by simple inspection, on the assumption that one bromo substituent deshields less than two, but more than one iodo.

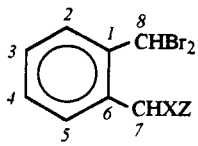
The ^{13}C signals for C-7 and C-8 were assigned by considering both electronegativity and heavy-atom effects on shielding (the complete ^{13}C NMR dataset is presented in Table 2, below). Thence, the assignments of the chemical shifts due to all the remaining protons and carbons became feasible on analyzing both short- and long-range proton-carbon correlation (HETCOR) experiments.



1a X = Br ; **1b** X = I ;



2a X = Br ; **2b** X = I ;



3 X = Z = H ;
4 X = H , Z = Br ;
5 X = Z = Br

Fig. 1. Structures and numbering for the *o*-xylene halo derivatives investigated.

Some aspects concerning the ^{1}H chemical-shifts of these halo compounds should be emphasized: (i) while the presence of a halogen atom attached to the benzylic carbon induces deshielding[8] of the *ortho* proton signals (H-2 and H-5, Table 1), this effect seems to be mainly due to the number of the halogen atoms present, and not to their nature (as can be seen by comparing data on compounds **1** and **2**); (ii) in all cases, the signals due to protons *ortho* to a halogen-bearing benzylic carbon appear to low field relative to the signals of all other aromatic protons; (iii) deshielding also occurs in at least one of the *meta* proton signals, when the molecule bears three or four bromo substituents.

Table 1. Assignments of the Experimental ^{1}H Chemical Shifts for *o*-Xylene Derivatives[a]

Compound[b]	H-2	H-3	H-4	H-5	H-7	H-8
1a	7.30	7.17	7.22	7.19	2.41	4.51
2a	7.34	7.28	7.28	7.34	4.67	4.67
3	7.80	7.18	7.24	7.06	2.38	6.86
4	7.92	7.38	7.25	7.22	4.55	7.08
5	7.64	7.36	7.36	7.64	7.14	7.14
1b	7.30	7.14	7.18	7.13	2.30	4.40
2b	7.29	7.20	7.20	7.29	4.55	4.55

[a] at 200 MHz, δ/ppm; TMS = 0.00; solvent: $CDCl_3$; [b] see **Fig. 1**.

On the other hand, in what regards the benzylic carbon signals in ^{13}C NMR (Table 2, assuming compound **1d**, *o*-xylene, as the reference), the inductive deshielding seems to dominate the δs of the bromo substituted compounds, while the heavy-atom effect shielding is dominant and intense for the iodo derivatives. The aromatic *ortho* carbon signals however, although generally more deshielded than the *meta* carbon signals, exhibit very small effects indeed. The same can be said about the *ipso* C-1/6 carbons which usually lie in the 135-140 ppm region except that the operation of γ-gauche shielding can be discerned at C-6, due to halogen substitution at C-8 for compounds **3** and **4**. Overall these effects are sufficiently small not to permit quantita-

tive generalizations to be made. The assignments are however very trustworthy for the protons and carbons because of the use of HETCOR experiments. We are also very confident in our assignments of the signals due to the quaternary (C-1/6) carbons, although it is possible to have them inverted, in the case of **1b**. On the other hand, the assignment of the signals for C-3/4 of compound **3**, while surprising, is the only possible interpretation of the HETCOR experiments for this compound and cannot be a mistake: C-3 really absorbs *ca.* 3 ppm downfield, relative to C-4, which is a break in the general trend for these two carbon signals in the molecules having no C_{2v} symmetry axis.

Table 2. Assignments of the Experimental ^{13}C Chemical Shifts for Halogenated *o*-Xylenes[a]

Cpd[b]	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
1a	136.86	129.66	126.06	128.60	130.43	135.40	18.41	32.18
1b	136.50	129.01	126.14	128.03	130.49	136.10	18.72	5.45
1c[c]	137.18	129.78	126.33	128.91	130.71	135.56	18.70	44.80
1d[d]	136.3	129.7	125.9	125.9	129.7	136.3	19.6	19.6
2a[e]	136.47	131.01	129.36	129.36	131.01	136.47	29.98	29.98
	(136.4)	(130.9)	(129.2)	(129.2)	(130.9)	(136.4)	(29.9)	(29.9)
2b	137.26	130.84	128.37	128.37	130.84	137.26	1.89	1.89
2c[f]	136.1	130.5	129.2	129.2	130.5	136.1	43.2	43.2
3	139.36	128.79	129.73	126.89	130.39	133.01	18.71	39.23
4	140.21	130.34	129.90	130.05	130.05	132.16	29.22	36.86
5[g]	137.55	129.30	130.30	130.30	129.30	137.55	36.49	36.49
	(137.6)	(129.3)	(130.2)	(130.2)	(129.3)	(137.6)	(36.4)	(36.4)

[a] at 50 MHz, δ/ppm; TMS = 0.00; solvent: $CDCl_3$; [b] Cpd = compound, see **Fig. 1**; [c] X = Cl, ref.5: spectrum S37054C (75 MHz); [d] X = H, ref.5: spectrum S4C (20 MHz); [e] in parentheses below, spectrum S7866C (20 MHz) from ref.5, for comparison; [f] X = Cl, ref.5: spectrum S19107C (20 MHz); [g] in parentheses below, spectrum S2648C (20 MHz) from ref.5, for comparison.

In order to obtain values for the proton-proton couplings it was necessary to refine the interpretation of the ^{1}H spectra by performing spectral simulations (using LAOCN9[9,10]) of the aromatic-proton region, for every compound (see Experimental section). The refined values of J obtained from the best-fit simulations, together with individual probable error (**pe**)[10,11] and global-fit rms error values, are presented in Table 3.

It must be pointed out that the refined output datasets contained δs identical (within ±0.02 ppm) to those initially input, taking the experimental uncertainity into account. For benzylic couplings (J_b), no values are presented in Table 3 because the best-fit results always were of the same magnitude as that of the corresponding probable error ($J_b \leq 0.30$ Hz $\approx$ **pe**). Hence if the J_b are not zero, they certainly are very small and, in fact, we verified that the inclusion or not of the J_b in the spectral simulations leads to equivalent results. The other coupling constants resulting from the best-fit calculations (Table 3) are in good agreement with the extant values[12] for other benzene derivatives.

In view of the probable errors found, we believe that most of the proton-proton coupling-constant data

are reliable enough. However, as in Table 3 there are four instances in which $^5J_{2,5} \approx$ **pe**, some considerations are due concerning the probable values these coupling constants should have. So, while for compounds **3** and **5** the actual value of $^5J_{2,5}$ should be zero, this is not the case for **1a** and **1b**, whose simulated spectra are critically sensitive to the value assumed by this parameter (acceptable results being obtained for $0 < |^5J_{2,5}| \leq 0.3$ Hz). A possible *ad hoc* rationalization for the $^5J_{2,5}$ values is to assume that $^5J_{2,5} = 0$ in *o*-xylene and that the substitution of benzylic proton by halogen-atom contributes with either 0.3 Hz (bromine) or 0.2 Hz (iodine) to that constant. The signal of this contribution depends on the relative angle between the C–X bond and the plane of the ring, in the predominant rotamer(s), through a Karplus-like function. Thence, all factors considered, the values of $^5J_{2,5}$ / Hz = 0.3 (**1a**); 0.6 (**2a**); 0.0 (**3**); -0.3 (**4**); 0.0 (**5**); 0.2 (**1b**) and 0.4 (**2b**) are fair estimations resulting from this model.

Table 3. Best-Fit Proton-Proton Coupling Constants[a] for *o*-Xylene Derivatives

Cpd[b]	$J_{2,3}$ ± pe[d]	$J_{2,4}$ ± pe[d]	$J_{2,5}$ ± pe[d]	$J_{3,4}$ ± pe[d]	$J_{3,5}$ ± pe[d]	$J_{4,5}$ ± pe[d]	rms[c] error
1a	7.58 ±0.17	1.63 ±0.03	0.17 ±0.17	7.71 ±0.03	1.62 ±0.02	7.63 ±0.03	0.15
2a	7.72 ±0.03	1.32 ±0.02	0.63 ±0.04	7.64 ±0.04	1.32 ±0.02	7.72 ±0.03	0.06
3	7.73 ±0.10	1.12 ±0.10	0.03 ±0.09	6.93 ±0.09	1.27 ±0.09	7.21 ±0.10	0.22
4	7.87 ±0.03	1.13 ±0.04	-0.31 ±0.04	7.63 ±0.05	1.21 ±0.06	7.79 ±0.04	0.07
5	7.94 ±0.06	1.31 ±0.06	-0.08 ±0.04	7.31 ±0.05	1.31 ±0.06	7.94 ±0.06	0.08
1b	7.66 ±0.14	1.35 ±0.11	0.23 ±0.15	7.36 ±0.13	1.51 ±0.08	8.04 ±0.12	0.25
2b	7.68 ±0.07	1.32 ±0.06	0.39 ±0.07	7.49 ±0.07	1.32 ±0.06	7.68 ±0.07	0.16

[a] J/Hz; data evaluated from simulations with LAOCN9[9,10]; [b] Cpd = compound, see **Fig.1**; [c] global-fit root-mean-square error; [d] **pe** = probable error[10,11] = 0.6745σ (σ is the standard deviation).

The global-fit rms error values (Table 3) indicate that very good fits were attained in some cases. Less satisfactory were the fits of the sub-spectra due to the α-monohalo derivatives (**1**), for which the best attainable resolution of ^{1}H NMR spectra is still insufficient for the observation of all single 56 lines of their ABCD sub-spectra. Moreover, in the case of the iodo compounds (**1b** and **2b**), it was utterly impossible to completely prevent some photolytical decomposition which, by generating (paramagnetic) free iodine atoms, led to the broadening of the observed signals. The sub-spectra from compounds **3**-**5** also present some broadened spectral lines due to the presence of conformational equilibria: for compound **3** this is a relatively small effect, but sufficient to degrade somewhat the simulation of the ABCX sub-spectrum; for compound **4** the effect is still small, and does not hamper the obtention of a good fit for its ABMX sub-spectrum; for compound **5**, however, a considerable broadening (see below) is observed in the *ortho* and benzylic proton signals, but as it exhibits an AA'XX' type sub-spectrum a good fit was still attainable. In fact this is the only case in the present work where analysis by direct methods[13] is straightforward: by assuming $J_{2,5} = 0$, one finds $J_{2,3} = J_{4,5} = 7.90$ Hz ; $J_{2,4} = J_{3,5} = 1.39$ Hz and $J_{3,4} = 7.40$ Hz , values in fair agreement with those obtained by simulation, if one takes the uncertainties to be ±0.06 Hz.

In the course of the present study, we found out that a ^{1}H DNMR investigation of compound **5** should be warranted because its room-temperature NMR spectra at 200 to 400 MHz present markedly broadened[14]

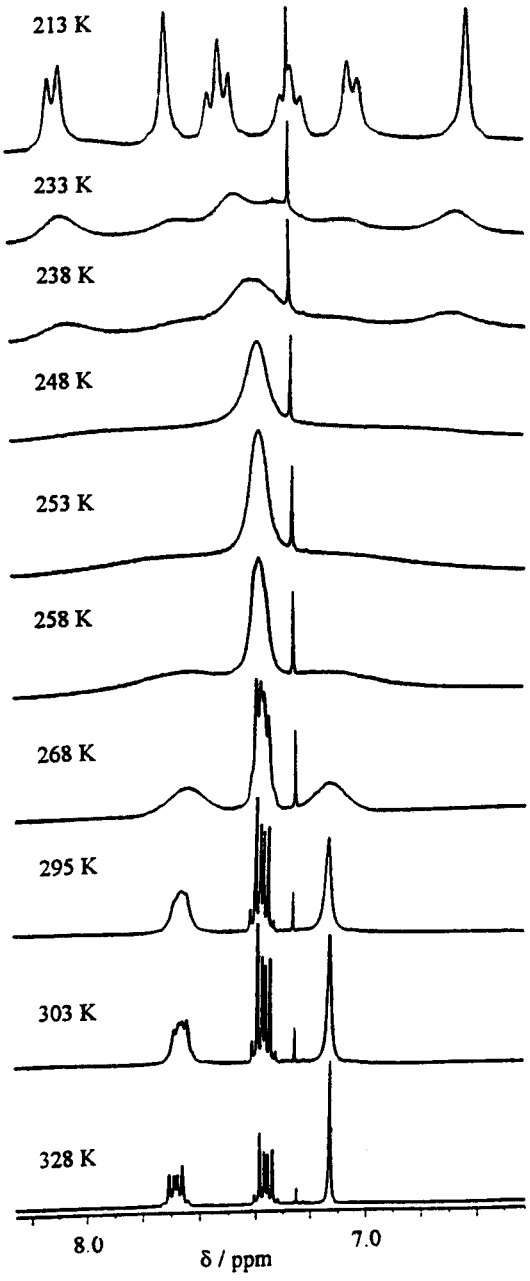


Fig. 2. ^{1}H NMR spectra of **5** in $CDCl_3$ at various temperatures.

ortho and benzylic proton signals as compared to the well-resolved spectra at 60 MHz, previously reported.[15a] Accordingly, we performed variable temperature experiments, some of which are shown in Figure 2. The same phenomenon is also observable in the ^{13}C NMR spectra from **5**. When our 50 MHz ^{13}C NMR spectrum of **5** is compared to the published 20 MHz spectrum,[15b] a conspicuous broadening is easily discernible in the signals due to the *ortho* and *ipso* carbons.

We found that on lowering the temperature, the proton spectra exhibit the expected changes and the complete resolution of all individual proton signals is attained at 213 K. Further cooling[16] to 208 K does not cause any other change to the observed spectrum. Hence, by performing a ^1H-{^1H} (2D) COSY experiment at 213 K we were able to assign all the observed signals which are: (δ/ppm) H-2 ⇒ 8.13; H-8 ⇒ 7.74; H-3 ⇒ 7.53; H-4 ⇒ 7.29; H-5 ⇒ 7.07; H-7 ⇒ 6.66, and (^{3}**J**/Hz), $\mathbf{J_{2,3}}$ = 7.76; $\mathbf{J_{3,4}}$ = 7.24; $\mathbf{J_{4,5}}$ = 7.47.

The only possible internal motions available to compound **5** happen to be rotations of the dibromomethyl substituents, which exert mutual hindrance to rotation, as they are in an *ortho* relationship. So, it seems reasonable to assume (by Occam's razor) that the spectrum obtained at T ≤ 213 K should be due mainly to the most stable of the rotamers and that, in view of the observed spectrum, it ought to be a rotamer with no C_2 axis. In our opinion the rotamer shown in Figure 3 (having C_s symmetry) is the most probable choice.[17]

Indeed, the rotamer in Figure 3 is consistent with the results of a series of a ^1H-{^1H} (1D) NOE difference experiments, performed at 213 K: on irradiation of H-5 (see **Fig. 3**) a 18% enhancement is observed on H-7 and, conversely, saturation of H-7 results on a 15% enhancement on H-5. Moreover, no relevant enhancements were observed on saturation of H-2 and none at all on irradiating H-8.

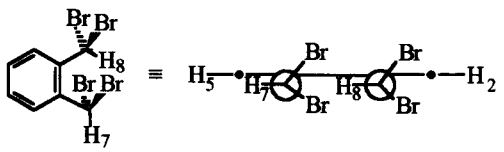


Fig. 3. Two different representations of the most stable rotamer proposed for **5**.

In this rotamer, we have H-8 surrounded by four bromine atoms, which point towards the part of the molecule where H-2 and H-3 are found. Thus these three protons are deshielded by the field effect exerted by those bromo substituents, while the other three protons, being at longer distances, are less influenced, absorbing to higher field. Hence, three different Δν (stemming from the same rotational interconversion) can be measured: 215.502 Hz, 213.395 Hz and 52.787 Hz for benzylic, *ortho* and *meta* protons, respectively.

As the benzylic protons give raise to singlets (see **Fig. 2**) we can calculate $\Delta G^{\neq}$ = (47.6 ±0.5) kJ mol^{-1} for the rotational interconversion at their coalescence temperature, (248 ± 2) K, using the approximation of Gutowsky and Holm[18a,b] (*i. e.*: $k_{coal.} = [\pi \Delta\nu]/\sqrt{2}$) and the Eyring[18a,b] equation, assuming the transmission coefficient κ = 1.

However, it is possible to evaluate $\Delta G^{\neq}$ at temperatures below coalescence, regardless of the multiplicities of the signals, by using both Eyring[18a,b] (with κ = 1) and Lozac'h[18a,c] equations. The latter equation yields more reliable values for the rotational constants because it relates them to changes in the intensities of the NMR signals (measured at each temperature) and to their width-at-half-height (measured only once, in the

absence of exchange), instead of to changes in bandwidth. In Table 4 we present the averages values of $\Delta G^{\neq}$ determined for each individual proton signal, at various temperatures, calculated through Eyring and Lozac'h equations, from the data in Table 5 (see Experimental).

Table 4. Mean Free Energies of Activation for the Rotation of $CHBr_2$ Groups in **5**, at Various Temperatures.

T/K →	243	238	233	228	223	218	213
$\Delta G^{\neq}$/ kJ mol^{-1} →	48.3	48.1	47.7	47.6	47.1	46.6	47.7

To our best knowledge, all previously published data[17] on the rotational barrier of α-halomethylbenzenes refers only to toluene derivatives ($\Delta H^{\neq}$/ kJ mol^{-1}: $PhCF_3$ ⇒ 1.0; $PhCCl_3$ ⇒ 1.3; $PhCHCl_2$ and $PhCH_2Cl$ ⇒ 4.2, both). Obviously, in those cases there is no steric hindrance due to the (absent) *ortho* substituent, so the data are not directly comparable, but led, assuming $\Delta H^{\neq} \approx \Delta G^{\neq} \approx$ 48 kJ mol^{-1}, to the estimation of the steric-hindrance contribution to the $\Delta H^{\neq}$ to be *ca.* 44 kJ mol^{-1}, *i.e.* about eleven times the contribution from the Pitzer strain. Further studies on similar compounds are presently under way.

EXPERIMENTAL

Materials

α-Bromo-*o*-xylene[19] (**1a**), α,α'-dibromo-*o*-xylene[20] (**2a**), α,α-dibromo-*o*-xylene[3] (**3**), α,α,α'-tribromo-*o*-xylene[21] (**4**), α,α,α',α'-tetrabromo-*o*-xylene[22] (**5**), α-iodo-*o*-xylene[23] (**1b**) and α,α'-diiodo-*o*-xylene[24] (**2b**) were prepared by literature procedures; all the solid compounds were then recrystalized from hexanes until colourless, while the liquids (**1a** and **3**) were distilled twice under reduced pressure just before use. The final purity attained for each one of these compounds was of at least 98% (both by GPC and by ^{1}H NMR analyses). **CAUTION!**: *All these compounds, especially the lower melting ones, are powerful lachrymators and must be handled with due care!*

Deuterochloroform (Aldrich) stored over 4Å molecular sieves was employed in all the experiments.

Instruments and Methods

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200-F equipped with an Aspect 3000 computer, an array processor and a variable-temperature probe, using DISNMR version 870101. Standard microprograms from Bruker Software Library were employed. All measurements were performed in 5 mm o.d. tubes, using a deuterium lock, at 20 °C, except where otherwise stated.

^{1}H spectra (200.13 MHz) were acquired with a sweep width 2202 Hz, giving a final digital resolution 0.134 Hz per data point. 32 scans were accumulated, using a pulse width of *ca.* 13°, with an acquisition time ≥ 7.4 s and a 10.0 s relaxation delay. Samples for ^{1}H spectra were prepared by dissolving *ca.* 50 mg of each *o*-xylene halo derivative in 0.5 mL of $CDCl_3$, containing 0.01 % ^{V}/v of TMS as internal standard.

Broadband ^{1}H decoupled ^{13}C spectra (50.32 MHz), were acquired with a sweep width ≥ 8000 Hz, giving a final digital resolution ≥ 0.488 Hz per data point. 64 scans were accumulated, using a pulse width of *ca.* 36°, with an acquisition time ≥ 1.0 s and no relaxation delay. Raw data were zero-filled and Fourier trans-

formed under matched-filter conditions. Samples for ^{13}C spectra and 2D experiments were prepared by dissolving *ca.* 250 mg of each *o*-xylene halo derivative in 0.5 mL of $CDCl_3$, containing 0.01 % V/v of TMS as internal standard.

HETCOR (^1H-^{13}C) experiments were performed using a low decoupler power in CW mode (composite phase decoupling) with polarization transfer from ^1H to ^{13}C. The FIDs for most 2D experiments were acquired with sufficient data points and numbers of evolution times to resolve all proton and carbon chemical shifts. Raw data were zero-filled in F1 and a gaussian window function was applied in both F1 and F2 prior to Fourier transformation. For one-bond and long-range proton-carbon coupling correlations, the delays were chosen to emphasize values of *ca.* 120 and 12 Hz, respectively.

The ^1H-{^1H} (2D) COSY experiment was performed using standard Bruker software. The NOE difference experiments were performed as described elsewhere.[25]

The 400.13 MHz spectrum of **1a** was acquired in a Bruker AVANCE DRX 400 with a sweep width 4310 Hz, giving a final digital resolution 0.066 Hz per data point. 16 scans were accumulated, using a pulse width of *ca.* 30°, with an acquisition time of 7.6 s and a 10.0 s relaxation delay.

Second-order ^1H NMR sub-spectra were analyzed using the program LAOCN9,[9] an IBM-PC compatible implementation of Laocoon-III.[10] The initial parameters employed were the δs measured either from the 1D proton spectra or from the HETCOR experiments (Table 1), and *reasonable estimates*[12] for the J values (*viz.* 7, 3, and 1 Hz, for *ortho*, *meta* and *para* couplings, respectively, and 0.5 Hz, for the benzylic one).

The $\Delta G^{\neq}$ were calculated by using both Eyring[18a,b] (with $\kappa = 1$) and Lozac'h[18a,c] equations as described by Sandström[18a] and Lozac'h *et al.*,[18c] using the data in Table 5, below, as the initial input.

Table 5. Amplitudes and Widths-at-half-height ($W_{½}$) of the signals in the ^1H NMR spectra of compound **5** (and of chloroform as the reference signal), at Various Temperatures.

Signal of →	H-2	H-8	H-3	H-4	H-5	H-7	$CHCl_3$
($W_{½}$ / Hz) →	(6.33)	(5.28)	(6.33)	(6.33)	(6.33)	(5.28)	(2.11)
T / K	Amplitude / cm						
243	1.10	-	-	-	-	1.10	9.00
238	1.70	-	-	-	-	1.60	10.00
233	2.40	1.80	3.90	3.20	1.60	2.10	10.00
228	4.00	2.90	5.35	4.30	2.70	3.80	11.70
223	5.00	4.50	6.30	4.50	3.80	5.10	12.10
218	5.60	6.50	7.10	5.20	4.80	7.10	12.10
213	7.30	11.70	9.20	6.80	7.10	11.70	12.00

All chromatographic analyses were performed on a Shimadzu CG-14-A gas chromato-graph, using a splitter injector (ratio = 43 : 1, temp. = 230 °C), a 25 m x 0.25 mm x 0.22 μm Shimadzu CBP-1 column (polydimethylsilicone), helium as carrier gas (flux: 1.6 mL/min), and a flame ionization detector (temp. = 260°C, nitrogen as make-up gas). Oven temperature program: 80 °C (for 4 min), 30 °C / min (up to 250 °C), 250 °C (for 2.7 min). Data was collected with a Shimadzu Chromatopac C-R4A electronic recorder / digital integrator.

Acknowledgments — Thanks are due to Mr. J. d. S. Malta Jr. and Mr. L. C. Roque for their technical assistance in the NMR experiments.

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8. unperturbed aromatic-proton signals from α-brominated *o*-xylenes should lie in the 7.17-7.19 ppm region, as can be discerned from the values of the signals of H-3/5 from **1a** and H-3 from **3**. The presence of a small deshielding of the signals due to the protons *para* to the brominated benzylic carbon and some shielding perceptible on the signal of H-5 from **3** hints at the presence of two effects: a through-bond inductive effect, operating also on the *para* protons, and a through-space, short-range field-effect, reaching the distal *ortho* proton. For the iodo compounds, use of similar reasoning leads to a 7.13-7.14 ppm region, for the unperturbed proton signal.
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11. the probable error is usually taken to be a fair estimate of the actual experimental uncertainity; actually, -0.6745σ is the lower quartile mark and $+0.6745\sigma$ is the upper quartile mark: the area under the normal distribution curve comprised between these marks is 50% of the total area.
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14. The width-at-half-height of the signal due to the benzylic protons is 2.2 Hz at 60 MHz (1.4 T); 5.3 Hz at 200 MHz (4.7 T) and 17.1 Hz at 400 MHz (9.4 T).
15. (a) ref. 7a, spectrum 2362M and ref. 7b, vol. 1, spectrum 783D; (b) ref. 5, spectrum S2648C.

16. Thanks to the cryoscopic lowering of the freezing point of deuterochloroform we were able to attain temperatures below 209 K (the m. p. of the pure solvent). The solution, however, becomes more and more viscous, what limits the spectral resolution.

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(*Received* 29 *January* 1997; *accepted* 27 *March* 1997)