An Assessment of Simple Theories of Chemical Shifts of Aromatic Protons as applied to Substituted Naphthalenes

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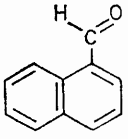
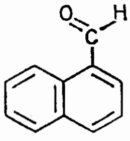
The proton chemical shifts of a number of 1-substituted naphthalenes are examined in the light of some of the simple theories of the origins of substituent chemical shifts claimed to be successful for benzene derivatives. It is shown that not one of these methods of predicting proton shifts gives correct answers for all positions in naphthalenes, and it is concluded that attempts to use proton shielding as an indication of molecular structure must be treated with caution. This point is illustrated by a discussion of the data for 1-naphthaldehyde, 2-hydroxy-1-naphthaldehyde, and 2-methyl-1-nitronaphthalene, and it is concluded that reliable structural information can be obtained only when changes in proton shielding can be ascribed to changes in the electron density on the proton.

THE effect of introducing a substituent into an aromatic compound is to produce large changes in proton shielding, and it was noted by Corio and Dailey[1] that for protons *para* to the substituent the changes paralleled the accepted changes in π electron density at the attached carbon atom. For the *ortho*-proton the chemical shift relative to benzene (which we will refer to as an SCS value) also followed π density changes on the *ortho*-carbon atom, although some substituents, such as the halogens, gave ' anomalous ' values. For *meta*-protons the SCS values were found to be of opposite sign to those expected on the basis of a correlation with carbon π density. Since this original observation there have been many attempts to quantify the relationship assumed between SCS values and carbon π densities, and to account for the deviations observed at *ortho*- and *meta*-positions.[2]

Our aim in this work is to examine the success of these relationships when applied to naphthalenes. Not only are monosubstituted naphthalenes a more severe test of any model for predicting proton shielding, but there are also structural problems associated with these molecules which it has been claimed can be resolved on the basis of proton SCS values. Thus the structure of 1-naphthaldehyde may be (I) or (II), or some equilibrium between the two. In both structures the molecule is assumed planar, as is the case for benzaldehyde. The true situation is likely to be rapid rotation about the C–C bond giving a probability distribution for the angle between the planes of the CHO and naphthalene ring which has maxima at positions corresponding to structures (I) and (II). We will, however, refer to the molecule being either (I) or (II) as a shorthand way of stating that the associated maxima in the probability distribution coincide with these structures and that either one or the other is more probable. N.m.r. evidence has been used to show that (II) is the only form in 4-methoxy-1-naphthaldehyde[3] by comparing the SCS value of the 8-proton in a number of aldehydes, and attributing a major part of the shift to the effects of the magnetic anisotropy of the CHO group. The conclusion here may be correct but the argument is not very strong, particularly when it is noted that the magnitude of magnetic anisotropy effects are obtained by assuming that for some test molecule the whole of the shift arises from this source, and that the formula used is itself invalid for short distances. It is also the case for the CHO group that different test molecules give opposite signs for the effect of magnetic anisotropy.[4,5] We have therefore examined other possible sources of the SCS value for the 8-proton and the calculated values of all the ring protons in both structures (I) and (II) will be compared throughout this paper. Also, we have partially analysed the spectrum of the 2-hydroxy-1-naphthaldehyde which could have the structure (III) because of a strong internal O–H $\cdots$ O hydrogen bond. A comparison of the 8-proton shift in this compound relative to 1-naphthaldehyde could reveal the possible structure of the aldehyde, provided the origin of the shift is understood.



(I)



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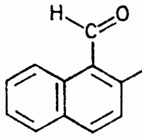

(III)

1-Nitronaphthalene is usually assumed to be planar, but 2-methyl-1-nitronaphthalene has been attributed a structure with the plane of the nitro-group perpendicular to the ring plane, again on the basis of comparing the shift of the 8-proton in the two molecules, and attributing any change to the change in the magnitude of the

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[1] P. L. Corio and B. P. Dailey, *J. Amer. Chem. Soc.*, 1956, **78**, 3043.

[2] T. B. Cobb and J. D. Memory, *J. Chem. Phys.*, 1969, **50**, 4262.

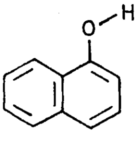
[3] W. B. Smith, D. L. Deavenport, and A. M. Ihrig, *J. Amer. Chem. Soc.*, 1972, **94**, 1959.

[4] G. J. Karabatsos, G. C. Sonnichen, N. Hsi, and D. J. Fenoglio, *J. Amer. Chem. Soc.*, 1967, **89**, 5067.

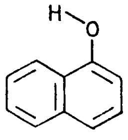
[5] J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, A. K. G. Nasser, L. Saunders, and W. B. Whalley, *Chem. Comm.*, 1966, 754.

magnetic anisotropy effect as the nitro-group moves out of plane.[6] We will first try out several ways of calculating the chemical shifts of the protons in 1-nitronaphthalene before deciding if the effect on the 8-proton shift of introducing a methyl group at the 2-position can be confidently attributed to the non-planarity of the molecule.

We have included three other molecules in this study whose structure is reasonably well known, so that the theories of chemical shifts can be widely tested. These molecules are α-naphthol, α-naphthylamine, and 1-methylnaphthalene. The molecule α-naphthol has of course a possibility, like the aldehyde, of existing as an equilibrium mixture of the two structures (IV) and (V), and we have accordingly calculated shifts for each structure. However, it turns out that the two structures give virtually indentical predicted shifts and hence in the Table only an average is presented. Similarly, 1-methylnaphthalene will show internal methyl rotation, and the calculated results are an average over two possible equilibrium geometries, one having a CH bond in the plane of the ring and pointing towards 8-H, and the other having it pointing towards 2-H. The two structures again do not show measurable differences. The probability distribution for methyl is such that strictly a weighted average of all structures should be taken, but we are confident that such a laborious process is unnecessary in this case because the proton shifts are not so sensitive to structure. The naphthylamine has been assumed planar, and for all the compounds the bond lengths and angles have been taken from the standard compilations.[7]



(IV)



(V)

Simple Theories of the Origin of Proton Shielding.—It is as well to stress that there is no problem of the origin of magnetic shielding. The Hamiltonian for a molecule in a magnetic field is well understood, and hence the computation of shielding constants can be done as accurately as the available wavefunctions allow. But of course the calculation of the wavefunction to sufficient accuracy is difficult, and has been attempted only for very small systems.[8] The problem really is how to calculate proton shielding without recourse to solving the full problem, but by making sweeping approximations, or even by simply observing correlations between chemical shifts and some other property of the molecular system. Such simple theories therefore cannot really contribute towards a true understanding of either chemical shifts or electronic structure, but they may serve to connect molecular or electronic structure to chemical shielding so that information useful in other contexts may be inferred with a high degree of probability. The examples of the structures of the naphthaldehydes are a case in point, but obviously the approach is liable to give misleading results if the connection is unreliable.

One approach towards obtaining simple relationships for proton shielding is the idea of Saika and Slichter.[9] that the shielding of a nucleus A, σ_A can be expressed as a sum of local contribution [equation (1) where

$$\sigma_A = \sigma_{AA}^{dia} + \sigma_{AA}^{para} + \sum_{B\neq A}(\sigma_{AB}^{dia} + \sigma_{AB}^{para} + \sigma_{A,\mathrm{deloc}} \qquad (1)$$

the superscripts *dia* and *para* refer to the division of the shielding constant into terms dependent on only ground state (*dia*) and on both ground and excited state wavefunctions (*para*) when perturbation theory is used]. The subscripts A and B refer to atomic centres such that σ_{AB} is the contribution of electrons on B to the shielding of A, and $\sigma_{A,\mathrm{deloc}}$ is the contribution to the shielding of A by electrons which cannot be described as localised on any atom. The relative magnitude of diamagnetic and paramagnetic terms depends upon the origin of the co-ordinate system used and when A is taken as origin the value of σ_{AA}^{dia} for protons is given by equation (2)

$$\sigma_{HH}^{dia} = \frac{e^2}{3mc^2} P_{1s1s} \left\langle \frac{1}{r} \right\rangle_{1s} \qquad (2)$$

where P_{1s1s} is the diagonal element of the charge density matrix corresponding to the 1*s* atomic orbital centred on hydrogen. The symbol $1/r_{1s}$ refers to the quantum mechanical average of $1/r$ for the electron in the 1*s* orbital, and if a Slater function is used to describe this then equation (2) becomes (3) where a_0 is

$$\sigma_{HH}^{dia} = \frac{e^2}{3mc^2}\frac{Z}{a_0}P_{1s1s} = 21\cdot34P_{1s1s} \qquad (3)$$

the Bohr radius and Z is the effective nuclear charge. The magnitude of this term for hydrogen in the hydrogen molecule is *ca.* 20 p.p.m., and variations in its magnitude account for most of the chemical shift difference between benzene and methane of 7·5 p.p.m. This corresponds to a change in P_{1s1s} of *ca.* 0·3 electrons, and is about that calculated by *ab initio* molecular orbital theories. Changes in P_{1s1s} will occur when a substituent is introduced into an aromatic molecule, but changes in σ_{HH}^{dia} have been neglected in most attempts to explain SCS values because of the difficulty of calculation for large molecules. It has been assumed that $\Delta\sigma_{HH}^{dia}$ is proportional to some other property such as the change in π electron density on the attached carbon atom or on a calculated change in electric field, or it has been assumed to be negligible. The magnitude of ΔP_{1s1s} for the 1-substituted naphthalenes relative to naphthalene has been calculated by the CNDO/2 method and the results of calculating $\Delta\sigma_{HH}^{dia}$ are shown in the Table. The most striking feature of these results is that for 1-nitronaphthalene the calculated values of $\Delta\sigma_{HH}^{dia}$ are

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[6] P. R. Wells, *Austral. J. Chem.*, 1964, **17**, 967.

[7] 'Interatomic Distances,' Supplements 11 and 18, 1958 and 1965, The Chemical Society, London.

[8] W. N. Lipscomb, *Adv. Mag. Resonance*, 1967, **2**, 138.

[9] A. Saika and C. P. Slichter, *J. Chem. Phys.*, 1954, **22**, 26.

very similar in magnitude to the observed shifts for all positions in the molecule, and on the evidence of this molecule it would be tempting to conclude that proton SCS values in aromatic molecules arise mainly from $\Delta\sigma_{HH}^{dia}$. But the results for other molecules in the Table do not support this view; indeed for many protons changes in $\Delta\sigma_{HH}^{dia}$ are either much smaller than the observed shifts, or are large but of opposite sign. It is clear that SCS values cannot be predicted by calculating only $\Delta\sigma_{HH}^{dia}$, however, if the accuracy of CNDO/2 wavefunctions is accepted then $\Delta\sigma_{HH}^{dia}$ is more reliably calculated than any other possible contribution *and cannot be ignored*. It is interesting to note therefore that the large low-field shift of the 8-proton in 1-nitronaphthalene almost certainly arises mainly from this source, and that structure (II) for 1-naphthaldehyde is predicted to have the 8-proton at −1·048 p.p.m. whereas structure (I) predicts that this proton will be at −0·128 p.p.m. from naphthalene.

Calculated and observed substituent chemical shifts for some 1-substituted naphthalenes

Proton	$\Delta\sigma_{HH}^{dia}$	σ_{mag}	$\Delta\sigma_{\pi}$ [a]	$\Delta\sigma_{\pi}$ [b]	$\Delta\sigma_{tot}$ [c]	$\Delta\sigma_{E}$	Δσ(obs) [17]
1-Nitronaphthalene							
2	−0·491	−0·152	−0·250	0·006	−0·106	−0·62	−0·807
3	−0·213	0·098	0·122	−0·072	0·036	−0·05	−0·146
4	−0·171	−0·046	−0·330	−0·190	−0·204	−0·20	−0·335 *
5	−0·064	−0·021	−0·028	−0·010	−0·028	−0·06	−0·195 *
6	−0·085	−0·003	−0·135	−0·135	−0·070	−0·11	−0·218
7	−0·128	0·032	−0·163	−0·195	−0·116	−0·14	−0·322
8	−1·346	0·210	−0·138	−0·124	0·213	−0·58	−0·725
1-Hydroxynaphthalene							
2	−0·256	−0·082	0·808	0·034	0·690	0·40	0·676
3	−0·042	0·000	−0·235	0·196	−0·210	−0·01	0·146
4	−0·010	0·005	0·438	0·270	0·300	0·23	0·357
5	−0·053	0·000	0·091	0·165	0·080	0·06	−0·012
6	−0·021	−0·002	−0·093	−0·030	−0·070	0·04	−0·031
7	−0·021	−0·019	0·115	−0·020	0·080	0·00	−0·064
8	−0·021	−0·159	−0·117	0·060	−0·175	−0·33	−0·410
1-Methylnaphthalene							
2	0·043	−0·017	−0·004	0·094	0·215	0·13	0·211
3	0·043	0·011	−0·106	0·066	−0·040	0·02	0·124
4	0·021	0·005	0·179	0·100	0·125	0·11	0·155
5	0·021	0·002	0·026	0·060	0·030	0·03	0·021
6	0·021	0·000	−0·021	0·003	−0·015	0·00	0·028
7	0·021	−0·007	0·040	0·010	0·025	0·02	0·006
8	0·000	−0·007	−0·005	0·035	−0·025	0·00	−0·110
1-Naphthaldehyde (I)							
2	−0·295	−0·091	−0·799	−0·518	−0·460	−0·63	−0·443
3	−0·128	−0·015	0·233	−0·206	0·300	0·15	−0·102
4	−0·085	−0·007	−0·481	−0·226	−0·210	−0·27	−0·218
5	−0·064	−0·005	−0·011	−0·001	0·090	0·08	−0·660
6	−0·107	0·005	0·104	−0·172	0·106	0·16	−0·147
7	−0·064	0·014	−0·073	−0·035	0·060	0·17	−0·237
8	−0·128	0·087	−0·045	−0·188	−0·130	−0·006	−1·525
1-Naphthaldehyde (II)							
2	0·235	0·055	−1·231	−0·835	−1·356	−1·72	−0·443
3	0·149	0·002	0·175	−0·420	0·130	−0·24	−0·102
4	0·107	−0·007	−0·643	−0·385	−0·470	−0·52	−0·218
5	0·000	−0·005	0·138	−0·046	−0·150	−0·14	−0·060
6	−0·064	0·002	0·111	−0·009	0·170	0·15	−0·147
7	−0·064	0·023	−0·103	−0·253	0·050	0·21	−0·237
8	−1·048	0·319	−0·173	−0·249	0·820	−0·65	−1·525
1-Naphthylamine							
2	−0·085	−0·014	0·882	0·360	0·650	0·45	0·766
3	0·042	0·002	−0·269	0·210	−0·190	0·01	0·164
4	0·021	0·003	0·510	0·310	0·340	0·28	0·507
5	0·021	0·001	0·090	0·190	0·090	0·11	0·052
6	0·000	−0·007	−0·080	0·004	−0·060	0·03	0·018
7	0·021	−0·005	0·125	0·036	0·080	0·04	0·009
8	0·063	−0·039	−0·100	0·080	−0·140	−0·14	0·060

[a] Calculated from the equation $\Delta\sigma_{\pi} = 10\Delta P_{\pi}$. [b] Calculated from equation (7). [c] Calculated from the equation $\Delta\sigma_{tot} = 10\Delta P_{tot}$.

* In ref. 17 these are incorrectly assigned.

The results in the Table indicate that with the possible exception of 1-nitronaphthalene the term $\Delta\sigma_{HH}^{dia}$ does not account for the observed shifts and other contributions to shielding must be large. The only other term in equation (1) which can be written in simple terms is the term $\sum_{B \neq A} (\sigma_{AB}^{dia} + \sigma_{AB}^{para})$ for the special case of a group of electrons centred on B which are remote from A. In this case the magnitude of this term is the well-known magnetic anisotropy effect, σ_{mag}, which is given by equation (4) where χ_B is the

$$\sigma_{mag} = -\frac{1}{3Nr_{AB}^3} [\chi_{Bxx}(1 - 3\cos^2\theta_{Bx}) + \chi_{Byy}(1 - 3\cos^2\theta_{By}) + \chi_{Bzz}(1 - 3\cos^2\theta_{Bz})] \quad (4)$$

magnetic susceptibility tensor for the group of electrons on B. The angle $\theta_{B\alpha}$ is that between the vector r_{AB} and the αth axis, and N is Avogadro's number. The difficulty in applying equation (4) is that values of χ_B are not known. Attempts have been made to derive the components of χ_B, but these usually involve assuming that the whole of some shift difference arises from a change in σ_{mag}. In the present case such an assumption clearly is inappropriate, and we have therefore calculated values of $\chi_{B\alpha\alpha}$ for the atoms in the substituent groups NO_2, CHO, OH, NH_2, and Me in the 1-substituted naphthalenes. To do this we have used the expressions developed by Pople[10] for the paramagnetic part of χ_B. In the CNDO/2 approximations the diamagnetic part of χ_B is isotropic and hence does not contribute to equation (4). Pople showed that χ_B^{para} is given approximately by (5) where ΔE is an

$$\chi_{Bxx}^{para} = \frac{Ne^2h^2}{4m^2c^2\,\Delta E} Q_{Bxx} \quad (5)$$

average excitation energy, and Q_{Bxx} is given by equations (6). The terms such as P_{yBzC} are elements of the charge

$$Q_{Bxx} = \sum_C Q_{BCxx}$$

$$Q_{BCxx} = P_{yByC}(\delta_{BC} - P_{zBzC}) + P_{zBzC}(\delta_{BC} - P_{yByC}) + 2P_{yBzC}P_{zByC} \quad (6)$$

density matrix, and in the present case have been calculated by the CNDO/2 method. The value of ΔE has been taken as 10 eV for all atoms, and the calculated values of σ_{mag} for the naphthalenes are shown in the Table. It is seen that the values of σ_{mag} are small except for protons near to the more anisotropic groups NO_2 and CHO. In these calculations σ_{mag} for the 2-proton in 1-nitronaphthalene is negative, but it is positive for the 8-proton. Similarly the value of σ_{mag} for the 8-proton in 1-naphthaldehyde is positive, and hence if these calculations are at all accurate it is clear that σ_{mag} cannot account for the large negative SCS values of the 8-protons in these molecules. The approximations in this method of calculating σ_{mag} are so large that the results must be treated as being unreliable, and it is our opinion that there is as yet no reliable way of calculating σ_{mag}, and that it is unwise to base structural arguments on the magnitude of this term.

We turn our attention now to examining methods of *predicting* proton SCS values by using empirically established correlations between shielding and other calculable properties of the molecule. The most favoured correlation has been between the SCS values and changes in π electron density on the attached carbon atom.[2] There is no obvious reason why proton shielding should be linearly related to π or total electron density on the attached carbon atom, but there is strong evidence that this is approximately true for the *para*-proton in substituted benzenes, and the proportionality constant is about 10 p.p.m. per electron. In an attempt to obtain an accurate value of this proportionality constant Fraenkel *et al.*[11] compared the proton shifts in the compounds $C_7H_7^+$, C_6H_6, and $C_5H_5^-$ since the π electron densities in these compounds are known from symmetry. Sebastian and Grunwell[12] have shown that the shift differences between these compounds are almost entirely accounted for by changes in σ_{HH}^{dia}, using CNDO/2 wavefunctions to calculate P_{1s1s}. It could be argued therefore that the observed correlations between π densities and SCS values simply reflects a proportionality between carbon π densities and P_{1s1s} for the electrons in a C–H bond. In the Table we show calculated SCS values in naphthalenes assuming linear relationships with either π or total electron density on the attached carbon atom. The CNDO/2 method does not give a proportionality between P_{1s1s} and P_π or P_{tot} and this can be seen by comparing columns 2, 4, and 6 in the Table. The SCS value for the 4-proton does show an approximately linear dependence on either π or total electron density at the attached carbon atom, but the magnitude of the SCS values predicted with a fixed value of the proportionality constant deviate substantially from the observed values in some compounds, and the relationship cannot therefore be used as an accurate indication of structure. For all other positions in the naphthalenes there is no indication of a simple relationship with either π or total electron density, and in particular the 8-proton in both 1-nitronaphthalene and 1-naphthaldehyde are predicted to have values very different from those observed.

A striking feature of calculated values of $\Delta\sigma_\pi$ for aromatic systems is that protons *meta* to a substituent are almost invariably predicted to have SCS values opposite in sign to those observed. This may arise from an incorrect method of calculating π densities,[13,14] but it has also been talen as an indication that the simple proportionality with π density on the attached carbon atom is inadequate for predicting proton SCS values. Shug and Deck[15] therefore included an extra term depending on the π density at next nearest neighbours [equation (7) where P_π^0, P_π^{+1} and P_π^{-1} are charge

$$\Delta\sigma_\pi = a_1P_\pi^0 + a_2(P_\pi^{+1} + P_\pi^{-1}) \quad (7)$$

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[10] J. A. Pople, *J. Chem. Phys.*, 1962, **37**, 53.

[11] G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, 1960, **82**, 5846.

[12] J. F. Sebastian and J. R. Grunwell, *Canad. J. Chem.*, 1971, **49**, 1779.

[13] J. W. Emsley, *J. Chem. Soc.* (*A*), 1968, 2523.

[14] K. Nishimoto, *Theor. Chim. Acta*, 1968, **10**, 65.

[15] J. C. Shug and J. C. Deck, *J. Chem. Phys.*, 1962, **37**, 2618.

density matrix elements for π orbitals on the attached and next neighbour carbon atoms]. The two constants a_1 and a_2 were suggested to be 7·1 and 2·9 p.p.m. per electron. Using this relationship for the naphthalenes gives the results shown in column 5 of the Table. Except for nitronaphthalene the 2-, 3-, and 4-protons have their shifts predicted reasonably well; however, this equation still fails to predict also the large negative SCS values of the 8-proton when the substituent is NO_2, CHO, or OH, and hence cannot be used to give structural information.

The correlation between the SCS value for the *para*-proton and ΔP_π in benzenes has been rationalised as being an example of the dependence of proton shielding on electric fields. A proton in a CH bond will have a change in its shielding if an electric field is applied along the bond direction,[16] and neglecting the small quadratic term the relationship is given by equation (8) where A

$$\sigma_E = -AE_Z \tag{8}$$

is calculated to be about 2×10^{-12} e.s.u. The difficulty in applying equation (8) lies in calculating E_Z within a molecule. If it is assumed that E_Z arises from point charges located on atoms, then E_Z will be given classically by equation (9) where q_B is the atomic charge,

$$E_Z = \sum_{B \neq A} q_B \cos \theta_{AB}/r_{AB}^2 \tag{9}$$

and can be equated to $(eP_{\text{total, B}})$. The angle θ_{AB} is that between the CH bond and r_{AB}. Of course, the true internal field is as difficult to calculate as the shielding constant and moreover, equation (9) is derived classically for a medium of unit dielectric coefficient, a concept meaningless within a molecule. It is therefore doubtful if equation (9) can be used to justify simple relationships with charge density matrix elements. Because of the difficulty of knowing how electric fields are transmitted within molecules we have restricted the summation in equation (9) to charges which neighbour the proton through space. The results of calculating $\Delta\sigma_E$ for the naphthalenes are shown in the Table where A has been given a value such that a charge of 1 electron a distance 1 Å away produces a shift of 10 p.p.m. The results show that this approach does reproduce some of the major features of the SCS values, such as the large negative values for the 2- and 8-protons in 1-nitronaphthalene and 1-naphthaldehyde [assuming structure (II) to be the only form present]. This method alone amongst those tried correctly predicts the shift of the 8-proton in all the molecules, including the large negative value for α-naphthol. The smaller shifts at the 3-, 5-, 6-, and 7-positions are not predicted with any accuracy.

Summary of Results for 1-*Substituted Naphthalenes.*—The results in the Table show that no one simple model can predict the SCS values of all the protons in these naphthalenes. But it is possible to predict some of the larger effects and to relate them to structure. Thus the magnitude of the 8-proton SCS value in 1-naphthaldehyde most probably is largely determined by $\Delta\sigma_{HH}^{dia}$ which predicts a shift for structure (II) of −1·048 p.p.m. and for structure (I) of only −0·128 p.p.m. compared with an observed value of −1·525 p.p.m. This is the strongest evidence from n.m.r. spectroscopy for the structure of this compound. The electric field model gives the best overall agreement with observed SCS values, and this model also favours structure (II) for the aldehyde on the basis of the value of the SCS value for the 8-proton, although in this case the agreement at the 2-position is not good and indeed favours (I) over (II).

2-*Hydroxy*-1-*naphthaldehyde.*—The proton spectrum of this compound dissolved in $CDCl_3$ has been analysed at 100 MHz. The lines arising from the 3-, 4-, and 8-protons are readily identified from INDOR experiments and yield the shifts relative to naphthalene of +0·299, −0·145, and −0·495 p.p.m. respectively. The shift of the 8-proton in 2-hydroxy-1-naphthaldehyde relative to 1-naphthaldehyde is therefore 1·030 p.p.m. and this is attributed to the change in the SCS value of the aldehyde group alone, *i.e.*, we neglect the effect of the OH group as such. That this is reasonable is supported by the spectrum of 2-hydroxynaphthalene, which even at 220 MHz is unresolvable, and shows that the effect of the OH group on the 8-proton is small. If it is assumed that 2-hydroxy-1-naphthaldehyde has structure (III) and 1-naphthaldehyde structure (II), then a CNDO/2 calculation gives a change in σ_{HH}^{dia} for the 8-proton as +1·012 p.p.m. Since the structure (III) is highly probable for 2-hydroxy-1-naphthaldehyde then the excellent agreement between the observed and calculated shifts can be taken as strong evidence for structure (II) for 1-naphthaldehyde. The changes in σ_π, σ_{total}, and σ_E for the 8-proton in going from structure (II) to (III) have been calculated and are $\Delta\sigma_\pi = 0{\cdot}490$, $\Delta\sigma_{\text{total}} = -0{\cdot}503$, and $\Delta\sigma_E = 0{\cdot}917$ p.p.m. Again, the electric field model also gives almost the correct magnitude.

2-*Methyl*-1-*nitronaphthalene.*—The proton spectrum of this compound dissolved in $CDCl_3$ at 100 MHz is badly resolved and only the shifts of the 3- and 4-protons can be clearly established, and are 0·162 and −0·045 p.p.m. respectively. The shift of the 8-proton cannot be obtained accurately but it can be assigned an approximate value of −0·04 to an accuracy of ±0·01 p.p.m. There is therefore a shift for the 8-proton of 0·77 p.p.m. in going from 1-nitro- to 2-methyl-1-nitronaphthalene. Again, this can be attributed entirely to the change in SCS value of the NO_2 group, as the shift of the 8-proton in 2-methylnaphthalene is only −0·025 p.p.m. different from that in naphthalene.[17] Assuming that 2-methyl-1-nitronaphthalene has a structure with the plane of the NO_2 group at right angles to the plane of the naphthalene ring, then a CNDO/2 calculation predicts a change of σ_{HH}^{dia} for the 8-proton of 1·04

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p.p.m. Calculated changes in σ_π, σ_{total}, and σ_E are $\Delta\sigma_\pi = 0{\cdot}187$, $\Delta\sigma_{\text{total}} = 0{\cdot}085$, and $\Delta\sigma_E = 0{\cdot}360$ p.p.m. The electric field model in this case is in the right direction but too small. The excellent agreement between $\Delta\sigma_{\text{HH}}{}^{dia}$ and $\Delta\sigma_{\text{obs}}$ for the 8-proton can again be taken as the strongest n.m.r. spectral evidence that introducing a methyl group into the 2-position changes the equilibrium position of the NO_2 group from coplanar to perpendicular with the plane of the aromatic ring.

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