fraction was determined at a total concentration of 0.2 g./5 ml. of carbon disulfide solution, with pure solvent in the reference cell. The concentration of the *meta* isomer was determined in concentrated solution by the method utilized in Procedure A. Summing up the results for the liquid fraction and the amount of the pure *para* isomer separated resulted in an analysis of 9.3% *ortho*, 1.52% *meta* and 89.2% *para*.

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Shifts in Nuclear Magnetic Resonance Absorption Due to Steric Effects. I. 2-Halobiphenyls

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A shift in proton resonance absorption toward higher field is observed for some of the protons in 2-halobiphenyls and is attributed to steric effects of the halogen upon the *ortho* protons of the unsubstituted ring.

Introduction

In 2-substituted biphenyls the benzene rings may be twisted out of a common plane if the 2-substituent is large enough. For the 2,2'-halobiphenyls this effect has been measured by electron diffraction experiments, and has been studied in terms of ultraviolet spectra and dipole moment data.[1-3] The angle between the benzene rings also has been determined for biphenyl and 2-fluorobiphenyl, and found to be the same within experimental error; but this angle has not been determined for the other 2-halobiphenyls.[1] This twisting of the benzene rings is required so that the *ortho* groups on the two rings do not overlap.

A proton resonance shift attributed to steric effects has been observed for the 4- and 5-protons in phenanthrene.[4] The aromatic rings are bent out of a common plane in order to avoid overlap of the 4- and 5-hydrogens. Since this situation is similar to that of the 2-substituted biphenyls, a proton resonance shift might also be expected in these compounds.

The proton magnetic resonance spectra of the 2-halobiphenyls and of the 4-halobiphenyls were obtained. It was hoped that any structure of the proton absorption signal due to electronic effects would be similar in both cases. Thus the change in the spectrum due to steric effects in the 2-substituted cases could be isolated.

Experimental

The nuclear magnetic resonance spectra were obtained with a Varian model V 4300B spectrometer equipped with an auxiliary stabilizer model VK 3506 and using a 12" Varian magnet. The samples were contained in cylindrical glass tubes having an inside diameter of 3 mm. The sample tubes were filled with about 0.4 cc. of sample and sealed, but the actual volume contained within the receiver coil was only 0.01 cc. The samples were rotated at a speed of 500–1500 r.p.m. to effectively improve the uniformity of the magnetic field. The spectrometer was operated at a frequency of 40 Mc. and a magnetic field of approximately 9400 gauss.

Measurements of the frequency shifts were obtained by superimposing an audio-frequency signal, from a Hewlett Packard model 200CD audio oscillator, upon the sawtooth sweep voltage applied to modulate the magnetic field.[5] This produced sidebands about the proton resonances with a separation corresponding to the frequency of the audio-oscillator. The spectra were recorded on a strip chart recorder and the separation of the sidebands used to calibrate the trace obtained. By this procedure the accuracy is thought to be about 1 cycle per second.

Relative intensities were obtained by cutting out and weighing the chart paper enclosed by the trace. It was found that different results were obtained from the Sanborn recorder supplied with the spectrometer (2" chart) and from a Leeds–Northrup Speedomax recorder (10" chart), although the results were reproducible for a given recorder. The intensities presented were obtained from the 10" chart.

Changing the bulk diamagnetism of a sample, and dilution in the case of aromatic compounds, may alter the position of the proton resonance absorption with respect to an absolute standard.[6] However, the measurements of interest in this study are the separation of closely adjacent peaks. Since they would be affected in a similar manner the separation between them would change very little. Therefore it is unnecessary to consider any changes due to differences in bulk diamagnetism or in concentration of the solutions. The spectra of 2-bromo- and 2-iodobiphenyl were obtained from the pure liquids, and that of 4-iodobiphenyl in a saturated dioxane solution. In the latter case the signal due to the solvent is sufficiently removed from the one due to 4-iodobiphenyl so that it is beyond the region shown in Fig. 2. The spectra of the other compounds were obtained in saturated carbon tetrachloride solutions. The magnetic field decreases from left to right in all spectra except 4-iodobiphenyl. In this case the field is increased to the right in order to avoid ringing from the very intense absorption due to the solvent.

Except for 2-fluorobiphenyl all the compounds studied were purchased from various chemical supply houses and used without further purification. There would be little effect due to small amounts of impurities since it is primarily the separation between the principal peaks which is of interest in this discussion.

2-Fluorobiphenyl was prepared by the Schieman reaction and had a m.p. 71–72°.[7]

Results

The significant features of the N.M.R. spectra are summarized in Table I. Δ is the difference in parts per million of the applied field between the observed peaks.

The fluorine resonance absorption of 2-fluorobiphenyl and 4-fluorobiphenyl are envelopes of width 24 cycles each or 0.60Δ unit.

For 2-chloro-, 2-bromo- and 2-iodobiphenyl, the intensity ratios of the peaks are 2:4.7, 2:5.3 and 2:8.2, respectively, compared to a theoretical ratio of 2:7.

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(1) O. Bastiansen, *Acta Chem. Scand.*, **8**, 1593 (1954).

(2) G. H. Beavan and D. M. Hall, *J. Chem. Soc.*, 4637 (1956).

(3) A. C. Littlejohn and J. W. Smith, *ibid.*, 2552 (1954).

(4) C. Ried, *J. Molec. Spectros.*, **1**, 18 (1957).

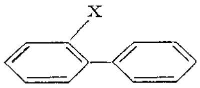
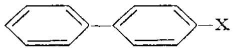
(5) J. T. Arnold and M. E. Packard, *J. Chem. Phys.*, **19**, 1608 (1951).

(6) A. L. Allred and E. G. Rochow, THIS JOURNAL, **79**, 5361 (1957).

(7) W. Rozelius and G. Schieman, *Ber.*, **62B**, 1805 (1929).

TABLE I

SEPARATION OF THE PROTON RESONANCE PEAKS IN SUBSTITUTED BIPHENYLS

Substituent		
H	1 peak	1 peak
F	2 peaks $\Delta = 0.18$	Envelope Width = $0.73\ \Delta$
Cl	2 peaks $\Delta = 0.21$	1 peak
Br	2 peaks $\Delta = 0.21$	1 peak
I	2 peaks $\Delta = 0.19$	3 peaks $\Delta = 0.20, 0.25$

Discussion

Biphenyl, 4-chloro- and 4-bromobiphenyl (Fig. 2) all show a single sharp peak due to proton resonance absorption. However, 2-chloro- and 2-bromobiphenyl have two principal peaks with a separation of 0.21 Δ unit (Fig. 1). If this were due to a shift in the resonance position of the *ortho* protons on the unsubstituted ring, relative intensities of 2:7 would be expected. The observed relative intensities are seen to bracket this value and their variation may possibly be due to different relaxation times.

The chemical shift between the peaks is of the same magnitude as the spin–spin coupling constants usually observed between *ortho* protons.[8] In such cases it is necessary to do a complete analysis using the 2nd order Hamiltonian to obtain accurate spin–spin coupling and chemical shift constants.[9] However, this analysis is quite complicated and has only been achieved in a five proton system where the chemical shift between the two main groups is 46 cycles.[10] Therefore it is impossible at present to do this when the separation is only 8 cycles and the assumption must be made that as a first approximation we may disregard the spin–spin coupling. The fine structure of the spectra is probably due to this coupling.

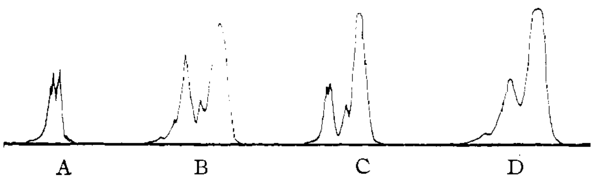


Fig. 1.—A, 2-fluorobiphenyl; B, 2-chlorobiphenyl; C, 2-bromobiphenyl; D, 2-iodobiphenyl.

The proton spectrum of 4-fluorobiphenyl (Fig. 2) is an envelope of peaks with a total width of 0.73 Δ unit. The fluorine resonance absorption gives an envelope of width 0.60 Δ unit so it is reasonable to assume that most of the line width in these cases is due to proton–fluorine spin coupling. In the absence of this effect the proton resonance spectrum of 4-fluorobiphenyl would probably be quite similar to that of 4-chloro- and 4-bromobiphenyl. The proton spectrum of 2-fluorobiphenyl (Fig. 1) has two peaks with separation 0.18 Δ unit and an envelope width of 0.63 Δ unit. The width of the fluorine resonance envelope, 0.60 Δ unit, is so close that one must assume a great deal of spin coupling between the protons and the fluorine nucleus. This makes it difficult to attribute the two peaks in the proton spectrum to a steric shift of the *ortho* protons. However, the similarity of the magnitude of this shift with those observed for the other 2-halobiphenyls is a strong indication of a similar origin.

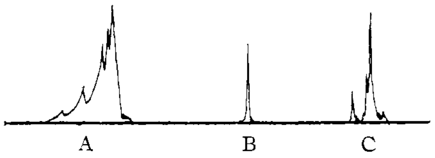


Fig. 2.—A, 4-fluorobiphenyl; B, 4-chlorobiphenyl; C, 4-iodobiphenyl.

The case of 2- and 4-iodobiphenyl is complicated by the fact that the spectrum of the 4-substituted compound (Fig. 2) has three peaks. Since iodine produces a greater chemical shift than the other halogens in halobenzenes,[11] a similar effect would be expected in halobiphenyls, and would account for the observed spectrum. However, the spectrum of 2-iodobiphenyl (Fig. 1) is very similar to those of the 2-substituted chloro and bromo compounds. It is not apparent why extra structure is not also observed in 2-iodobiphenyl but the marked similarity of its spectrum and the other 2-halobiphenyls suggests that the chemical shift, yielding two principal peaks, occurs for the same reason.

Another possible explanation for the observed spectra would be to consider the two peaks to be due to the protons on the substituted, and the unsubstituted, benzene rings. However if this were true one would expect similar spectra for both the 2- and 4-substituted compounds. A greater chemical shift would be expected with increasing atomic number of the halogen,[11] which is not observed. Therefore this explanation seems unlikely.

If sufficient information were available, the spectra could in principle be explained by a consideration of the diamagnetic anisotropies of the various atoms.[12] Since the difficulties in calculation increase rapidly with more complex molecules it would seem valuable to apply instead the concept of steric effects which, although more qualitative, has been well established in many other situations.

Since the benzene rings would have a maximum resonance energy when coplanar it is reasonable to assume that this tendency to coplanarity will cause the *ortho* hydrogen and halogen atoms to be in van der Waals contact. On this assumption one may calculate the angle between the benzene rings in the 2-halobiphenyls and these results are listed in Table II. The angles for biphenyl and 2-fluorobiphenyl agree with those experimentally determined, and with previous calculations.[1,2]

The melting points of these compounds are also explained by the twisting of the rings as the size of

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[8] H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, THIS JOURNAL, **79**, 4596 (1957).

[9] H. J. Bernstein, J. A. Pople and W. G. Schneider, *Can. J. Chem.*, **35**, 65 (1957).

[10] H. J. Bernstein, J. A. Pople and W. G. Schneider, *Can. J. Chem.*, **35**, 1487 (1957).

[11] P. L. Corio and B. P. Dailey, THIS JOURNAL, **78**, 3043 (1956).

[12] H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

TABLE II

TWISTING OF THE BENZENE RINGS IN 2-HALOBIPHENYLS

Substituent	C–halogen bond length,[a] Å.	van der Waals radius,[b] Å.	Angle[c]
H	1.04	1.20	42
F	1.35	1.35	49
Cl	1.69	1.80	64
Br	1.88	1.95	67
I	2.00	2.15	72

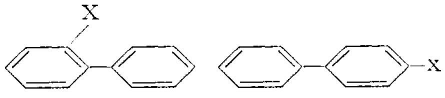
[a] Electron Diffraction; P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950). [b] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 2nd ed., 1942, p. 189. [c] The distance between the rings is taken to be 1.50 Å., the carbon bond length 1.40 Å., and no deformation of the bonds is assumed.

the 2-substituent is increased. An increase in melting point would be expected with increasing molecular weight, and this is found for the 4-halobiphenyls. The melting point of the 2-halobiphenyls decreases as the molecular weight increases. This may be caused by the decreasing symmetry of the molecule as the benzene rings are twisted further out of plane. This is shown in Table III.

Conclusion

TABLE III

MELTING POINTS OF 2- AND 4-HALOBIPHENYLS[a]



Substituent	M.p., °C.	M.p., °C.
H	69	69
F	71	74
Cl	34	76
Br	−20	89
I	Liquid	113

[a] These values are taken from Beilstein's "Handbuch der Organischen Chemie."

Steric repulsion, as found between the halogen and *ortho* hydrogens in a 2-halobiphenyl, may cause a shift in the nuclear magnetic resonance absorption of the hydrogen atoms concerned. Examination of the spectra of model compounds makes it appear unlikely that the change in the resonance absorption is due to electronic effects.

Acknowledgment.—The author wishes to thank Professor R. Bersohn for many helpful discussions.

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[CONTRIBUTION FROM THE PHYSICAL RESEARCH SECTION, UNITED STATES BUREAU OF MINES]

Some Salts of Nitrocyanamide and their Efficiency as Primary Explosives

BY SAMUEL R. HARRIS

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The preparation and isolation of nitrocyanamide and some of its salts are described. A number of the latter have been subjected to tests designed to determine their adaptability as initiating explosives.

Introduction

During an investigation of the use of N-alkyl-N-nitroso-N′-nitroguanidines in the preparation of diazohydrocarbons, McKay[1] isolated potassium nitrocyanamide as a by-product. He noted that, when heated above its melting point on a spatula, this salt exploded and could be readily detonated by the blow of a hammer. These explosive properties of potassium nitrocyanamide aroused interest in the possibility that some other salts of nitrocyanamide might be even more susceptible of initiation to detonation. Considering the pressing need for more efficient primary explosives, this investigation was aimed primarily at preparing some of the heavier metal salts of nitrocyanamide to test their suitability as initiating explosives.

The various salts of nitrocyanamide were generally prepared by a metathetical reaction between silver nitrocyanamide[2] and the appropriate metal chloride in a suitable solvent. Alternatively, a number of the salts were prepared by treating the solid metal carbonates with a solution of nitrocyanamide in acetonitrile. This method proved particularly clean-cut.

Most of the nitrocyanamide salts prepared were readily eliminated from serious consideration as useful primary explosive compounds because they proved too insensitive to impact when tested upon the Bureau of Mines impact machine. These included all salts prepared, except those of potassium, tin, lead, barium, and silver. None of the others were detonated by the impact of a 5-kg. weight falling through a distance of 300 cm. A contributing factor to this insensitivity to impact may have been either hygroscopic moisture or water of crystallization. Each of the insensitive salts tested was hydrated, hygroscopic or both. Although the potassium salt could be consistently detonated by the impact of a 5-kg. weight falling from a height of 125 cm., this was well outside the impact sensitivity range of the commonly used primary explosives and thus it was eliminated. The tin and lead salts, though quite sensitive to impact when vacuum-dried over a desiccant, readily picked up enough moisture on short exposure to the atmosphere to greatly reduce their sensitivity to impact. This shortcoming was enough to remove them from any further consideration as practical primary explosive compounds.

A rather graphic illustration of the effect of hygroscopicity and/or water of crystallization upon impact sensitivity was obtained when the two lead salts and the tin salt of nitrocyanamide were tested

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(1) A. F. McKay, *et al.*, *Can. J. Research*, **28B**, 683 (1950).

(2) A. F. McKay, W. G. Hatton and G. W. Taylor, unpublished data.