

difference obtained by subtracting the two independently measured values.

The aromatic proton resonance of the *cyclopropanes*, *trans*-diphenylcyclopentane, *cis*-stilbene and meso-diphenylbutane appeared as a sharp singlet in each case. *cis*-Cyclopentane and *trans*-stilbene had their aromatic proton resonance maxima separated into doublets with the separation between the peaks not more than 4 and 1.5 c.p.s., respectively. The position of the absorption was considered to be a point at one-half of the distance between the peaks. The azobenzenes caused more difficulty since their aromatic proton resonance was resolved into two groups of peaks, the centres of which were separated by some 11 (*cis*) to 21 (*trans*) c.p.s. Here a point one-half the distance between the centres of the two groups was arbitrarily taken as the position of the resonance. Consequently, it is clear that the separation of +23 c.p.s. reported in Table I is subject to considerable uncertainty. All the α -hydrogen resonances except for the stilbenes appeared as incompletely resolved multiplets and the centres of these multiplets are given in Table I.

It is seen that the aromatic protons of the *cis* partners are more shielded than those of the *trans*, although unfortunately, the difference is not sufficiently dependent on ring size to permit a correlation with the change in molecular geometry due to the change in ring size. The shifts of the α -hydrogen frequencies of the *cycloalkanes* are in the same sense, the proton *cis* to the adjacent phenyl group (*trans* isomer) giving rise to resonance at higher field than when it is *trans* (in the *cis* isomer). The positions of both the aromatic and α -proton resonances of meso-2:3-diphenyl butane are similar to the *trans* cyclopentane and suggest that this molecule exists largely in the *trans* conformation as might be expected from a consideration of molecular models. It should be noted that the α -hydrogens are reversed in the case of the stilbenes.

Although the source of such shifts may be more subtle (and probably is, at least in the case of the olefinic hydrogens of the stilbenes) it seems possible that these are internal examples of the shifts previously found as intermolecular effects of aromatic solvents,⁵ resulting from the electron supercurrent of the aromatic ring.⁵⁻⁷

The shifts of the aromatic and α -proton resonance positions in 2:2-paracyclophane are in the same direction although somewhat larger than those found in the cyclopropane and cyclopentane systems. Waugh and Fessenden,⁷ however, concluded on the basis of calculations that the diamagnetic ring moment was not responsible for the paracyclophane shifts but that instead they must be attributed to distortion of the aromatic rings. This distortion is, of course, not present in the diphenylcyclopropanes and cyclopentanes discussed here.

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INTRAMOLECULAR HYDROGEN BONDING IN *O*-NITROANILINE

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The recent paper on intramolecular hydrogen bonding in *o*-nitroanilines¹ prompts us to report some results of our own investigation on this problem.

We have examined the infrared absorption spectra of *o*-, *m*- and *p*-nitroanilines in solution (0.05%) in carbon tetrachloride. A Hilger H-668 single beam spectrophotometer with sodium chloride prism was used.

The frequency ranges 2, 5-4 μ (N-H stretching frequencies) and 7.0-8.0 μ (NO_2 symmetric stretching vibrations) were examined. Nitro group asymmetric vibrations near to 6.0 μ were not examined owing to overlapping with carbon tetrachloride bands.

It has previously been found by one of us,² that in aliphatic nitro compounds the hydrogen bonds reduce both frequencies of the nitro group vibrations.

Thus, the symmetric stretching frequencies 1361-1340 cm^{-1} have been reduced to 1319-1310 cm^{-1} under the influence of the hydrogen bond.

The following frequencies have been now found in all three isomeric nitroanilines:

	N—H frequencies cm^{-1}		NO_2 symmetric frequencies cm^{-1}
<i>o</i> -nitroaniline ..	3510	3390	1350
<i>m</i> -nitroaniline ..	3510	3450	1350
<i>p</i> -nitroaniline ..	3510	3450	1340

The frequencies of N-H stretching vibrations agree with those given by literature and found by Dyal and Hambly.¹

The frequencies of the nitro group symmetric vibrations agree with data for a free, unbonded nitro group.

Thus, we have not found any evidence of the existence of a hydrogen bond between the amino and nitro groups of *o*-nitroaniline.

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References

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ATOMIC ENERGY AGREEMENT

The U.K. Atomic Energy Authority have concluded a 5-year agreement with Power Reactor Development Company of Detroit, U.S.A., for the exchange of information concerning the development of fast reactors.