

contribution to the substituent constant.⁴ For the nitro group these values are +1.27 and +0.63,⁴ so that a noncoplanar nitro group at C-2 should reduce ground-state electron density on the amine function by about half the extent of a coplanar nitro group.

It is a constructive exercise to assume that the 2-nitro group is completely coplanar in 2,4-dinitroaniline and completely noncoplanar in N,N-diethyl-2,4-dinitroaniline. The blue shifts caused by this substituent in the maxima of the former compound relative to 4-nitroaniline and the latter compound relative to N,N-diethyl-4-nitroaniline should then be proportional to σ_{para}/σ_1 . As an independent check of our reasoning, we may compare the observed position of the maximum for V with λ_{max} predicted as follows.

For 4-nitroaniline, $\nu_{max} = 26,950 \text{ cm.}^{-1}$; for 2,4-dinitroaniline, $\nu_{max} = 29,760 \text{ cm.}^{-1}$; effect of coplanar 2-nitro group = +2810 cm.^{-1} . For N,N-diethyl-4-nitroaniline, $\nu_{max} = 25,410 \text{ cm.}^{-1}$; predicted effect of noncoplanar 2-nitro group = $(0.63/1.27)(2810) = +1390 \text{ cm.}^{-1}$. This leads to a prediction of $\nu_{max} = 26,800 \text{ cm.}^{-1}$ for N,N-diethyl-2,4-dinitroaniline, corresponding to $\lambda_{max} 373.5 \text{ m}\mu$. The observed position for V is 375 $\text{m}\mu$.

The Electronic Buttressing Effect.—A further difference between several of the spectra discussed above deserves additional comment. It has been mentioned that, on dimethylation of 2-nitroaniline, reduction by somewhat less than half in the ($+R_2N=C_1 \rightarrow C_2=NO_2^-$) absorption intensity was observed, but that on dimethylation of I the corresponding band appeared to vanish completely. To confirm that band 1 in compound IV was not disturbed on its longer wave length side by any absorption attributable to band 2, the band half-widths at half-height on both sides of the maximum were compared. The values were: from ν_{max} to the blue, 2700 cm.^{-1} ; from ν_{max} to the red, 2400 cm.^{-1} ; *i.e.*, disturbance of the symmetry of the band, if any, was on the shorter wave length side and was probably due to slight overlap with the tail of a shorter wave length band. A putative explanation for this difference in behavior in N,N-dimethylation is as follows.

Steric strain in N,N-dimethyl-2-nitroaniline may be relieved by rotation from planarity of either the Me_2N-

or the NO_2- group or by increasing the $(Me_2)N-C_1-C_2$ angle or the $C_1-C_2-N(O_2)$ angle or by any combination of these possibilities. An energetically preferred conformation would probably find this compound with both the NO_2- group and the Me_2N- group partially noncoplanar, *i.e.*, partial $\pi-\pi$ overlap between nitro and ring, partial $p-\pi$ overlap between amino and ring. The ($+R_2N=C_1 \rightarrow C_2=NO_2^-$) band is still evident, but with decreased absorption intensity following the $[\cos^2 \theta = \epsilon/\epsilon_0]$ relationship.¹²

In the case of N,N-dimethyl-2,4-dinitroaniline, rotation from planarity of the amine function would strongly decrease ($+R_2N=C_1 \rightarrow C_4=NO_2^-$) resonance interaction, so that conformations involving rotation or bond distortion of the amine group would be energetically less favored than had been the case in the absence of the 4-nitro substituent. Relief of steric strain would then require greater rotation from planarity of the 2-nitro substituent, decreasing its $\pi-\pi$ overlap with the ring to a very much greater extent; $\cos^2 \theta$ would approach zero and the band would virtually disappear.

If this explanation for these spectral differences applied, the action of the 4-nitro substituent in decreasing coplanarity of the 2-nitro substituent by "stiffening" the 1-dimethylamino substituent might be termed an *electronic buttressing effect*.

Experimental

All materials were commercially available or prepared by literature methods. They were purified by standard means to meet conventional spectrophotometric criteria of purity. Absorption spectra were determined in methanolic solution using a Cary Model 14 recording spectrophotometer with matched 1-cm. silica cells. Concentrations were $3-5 \times 10^{-6} M$. Previously described precautions¹³ were taken to guard against photochemical transformations.

Acknowledgments.—Helpful discussions with Mr. D. J. Glover and Drs. T. N. Hall, D. V. Sickman, and J. C. Dacons are gratefully acknowledged. The work was done in part under NOL Task FR-44 and in part while M. J. K. was attached to the Embassy of the United States, Office of Naval Research, London.

(12) E. A. Braude in E. A. Braude and F. C. Nachod, Ed., "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 174.

(13) M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MOUNT HOLYOKE COLLEGE, SOUTH HADLEY, MASS.]

Substituent Effects on Nuclear Magnetic Resonance Chemical Shifts in *para*-Substituted Phenylhexachlorobicyclo[2.2.1]heptenes and Ethylbenzenes¹

BY KENNETH L. WILLIAMSON, NANCY CRAVEN JACOBUS, AND KAREN TABOR SOUCY

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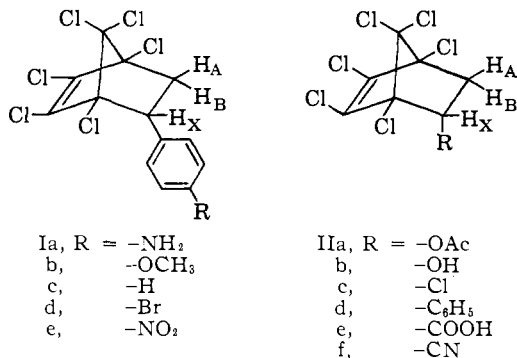
The internal chemical shifts in a series of *para*-substituted 5-phenylhexachlorobicyclo[2.2.1]heptenes have been found to be independent of dihedral angle, in contrast to 5-substituted hexachlorobicyclo[2.2.1]heptenes. The chemical shifts of the aliphatic protons in the bicyclic series as well as the chemical shifts of the methyl and methylene protons in *para*-substituted ethylbenzenes have been correlated with the Hammett σ -constant of the substituent.

The purpose of the work reported herein was to determine whether an angular dependence of the internal

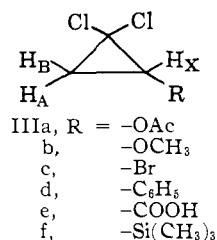
chemical shifts of the aliphatic protons would be noted in the series of *para*-substituted 5-phenylhexachlorobicyclo[2.2.1]-2-heptenes (1a-e). It has previously been shown² that the internal chemical shifts, $\delta_X - \delta_A$

(1) This work was supported by grants from the Public Health Service, Division of General Medical Sciences (GM10224-01), and from the Petroleum Research Fund of the American Chemical Society.

(2) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963).



and $\delta_X - \delta_B$, between the X and A or B protons in the series of 5-substituted hexachlorobicyclo[2.2.1]-2-heptenes (IIa-f) is markedly dependent on both the electronegativity of the group R and on the dihedral angle between the C-R bond and those bonds involving the adjacent (A or B) protons.³ Exactly the same effect has been noted for the series of monosubstituted 1,1-dichlorocyclopropanes (IIIa-f).⁴



In our previous work we have used as our definition of substituent electronegativity the relation proposed by Cavanaugh and Dailey⁵: electronegativity = $0.0114\delta + 1.78$ where δ is the internal chemical shift in c.p.s. at 60 Mc. between the methyl and methylene protons in a series of monosubstituted ethanes. This definition of the relative electron-withdrawing and -donating properties of a substituent is based entirely on the nuclear magnetic resonance experiment. However, in the present work dealing with a series of *para*-substituted phenyl derivatives, we might expect to be able to correlate chemical shift data with the corresponding Hammett σ -constants⁶ for the various substituents. A number of studies of substituent effects on the n.m.r. chemical shifts of protons bound directly to the benzene ring has been reported.⁷⁻¹⁶ Lauterbur¹⁷ has similarly studied substituent effects on the ring carbon chemical shifts, and Gutowsky¹⁸ and Taft^{19,20} substituent effects

on aromatic fluorine resonance shifts. Most of this work has been summed up by Spiesscke and Schneider¹⁴ who showed that there is a general correlation of *p*-hydrogen, as well as C^{13} and F^{19} , chemical shifts with the corresponding Hammett σ -constants of substituents.

Only recently have the effects of substituents on the chemical shifts of protons not directly bound to the aromatic ring been studied. Klinck and Stothers²¹ found a rough correlation between the chemical shift of the formyl proton in a series of aromatic aldehydes and the corresponding Hammett σ -constant.

Paterson and Tipman,²² studying some *para*-substituted phenols, found that the hydroxyl proton chemical shift at infinite dilution in carbon tetrachloride was almost independent of the nature of the ring substituent. However, Heathcock,²³ in studying a much larger series of *para*-substituted anisoles, found a reasonably good correlation between the methyl resonance and the corresponding Hammett σ -constant. A comparison of these two studies reveals that the infinite dilution work done on the phenols probably did not embrace a wide enough range of electron-donating and -withdrawing substituents to draw a valid conclusion regarding substituent effects.

The acetylenic proton chemical shifts for a series of *para*-substituted phenylacetylenes have been found by Cook and Danyluk²⁴ to give a good linear correlation with a combination of inductive and resonance σ -constants.

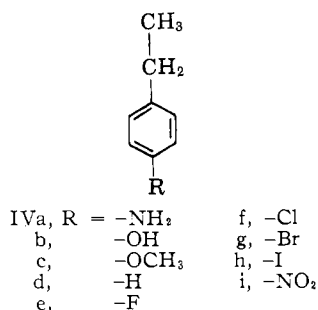
Jackman²⁵ has reported the chemical shifts of the methyl group in some *para*-substituted toluenes, but he does not comment on these other than to say that only the more powerful electron-withdrawing nuclear substituents significantly alter the methyl group resonance frequency.

In the present work we expected to be able to correlate the chemical shifts of the three aliphatic protons on the bicyclic system with the Hammett σ -constant of the substituent in the *para* position of the phenyl ring. The bicyclic ring system used in this study has several advantages: there are only three coupling protons in the aliphatic region of the spectrum facilitating complete, unambiguous analysis of the spectra; the three protons are fixed in their relationship to each other with a known (120°) dihedral angle between the *trans* protons; and finally a variety of electron-withdrawing and -donating substituents are easily introduced into the *para* position of the phenyl group. In order to determine the effect of the highly halogenated ring system on these protons (other than holding them in a rigid relationship to each other) we also examined the chemical shifts of the methyl and methylene protons in a series of *para*-substituted ethylbenzenes (IVa-i).

In Table I are listed chemical shifts of the A, B, and X protons for the *para*-substituted phenylbicycloheptenes (Ia-e). These data were calculated by an ABX analysis²⁶ of the spectra.

- (3) See Fig. 4 of ref. 2.
 (4) K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *J. Am. Chem. Soc.*, **86**, 762 (1964).
 (5) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961).
 (6) L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 96 (1937).
 (7) P. L. Corio and B. P. Dailey, *ibid.*, **78**, 3043 (1956).
 (8) A. A. Bothner-By and R. E. Glick, *ibid.*, **78**, 1071 (1956).
 (9) A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).
 (10) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Am. Chem. Soc.*, **81**, 5352 (1959).
 (11) I. Yamahuchi and N. Hayakawa, *Bull. Chem. Soc. Japan*, **33**, 1128 (1960).
 (12) R. R. Fraser, *Can. J. Chem.*, **38**, 2226 (1960).
 (13) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).
 (14) H. Spiesscke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).
 (15) P. Diehl, *Helv. Chim. Acta*, **44**, 829 (1961).
 (16) B. P. Dailey, A. Gawer, and W. C. Neikam, *Discussions Faraday Soc.*, **34**, 18 (1962).
 (17) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1846 (1961).
 (18) H. S. Gutowsky, D. W. McCall, B. R. McGarvey, and L. H. Meyer, *J. Am. Chem. Soc.*, **74**, 4809 (1952).
 (19) R. W. Taft, Jr., *ibid.*, **79**, 1045 (1957).

- (20) R. W. Taft, Jr., R. E. Glick, I. C. Lewis, I. R. Fox, and S. Ehrenson, *ibid.*, **82**, 756 (1960); R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 709, 3146 (1963).
 (21) R. E. Klinck and J. B. Stothers, *Can. J. Chem.*, **40**, 1071 (1962).
 (22) W. G. Paterson and N. R. Tipman, *ibid.*, **40**, 2122 (1962).
 (23) C. Heathcock, *ibid.*, **40**, 1865 (1962).
 (24) C. D. Cook and S. S. Danyluk, *Tetrahedron*, **19**, 177 (1963).
 (25) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 58.



In Table II are listed chemical shifts for the aliphatic protons in the series of *para*-substituted ethylbenzenes. A first-order approximation was used to obtain the chemical shifts, *i.e.*, the center line of the methyl triplet and the average of the two center lines of the methylene quartet were taken as the chemical shifts for the methyl and methylene protons, respectively.

TABLE I
 CHEMICAL SHIFTS^a FOR *para*-SUBSTITUTED
 PHENYLHEXACHLOROBICYCLOHEPTENES (I)

Substituent, R	δ_A	δ_B	δ_X	σ_P^b
Ia, -NH ₂	136	168	225	-0.66
b, -OCH ₃	139	171	231	-0.268
c, -H	143	173	236	0.000
d, -Br	140	173	234	+0.232
e, -NO ₂	146	178	245	+0.778

^a Chemical shifts are given in c.p.s. downfield from internal tetramethylsilane at 60 Mc. ^b Hammett *para*-substituent constants based on the ionization of substituted benzoic acid as reported by D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

TABLE II
 CHEMICAL SHIFTS^a FOR *para*-SUBSTITUTED ETHYLBENZENES (IV)

Substituent, R	δ_{CH_3}	δ_{CH_2}	σ_P^b
IVa, -NH ₂	68.0	147.0	-0.66
b, -OH	68.0	150.5	-0.37
c, -OCH ₃	69.5	151.0	-0.268
d, -H	72.0	155.5	0.000
e, -F	72.0	155.0	0.062
f, -Cl	73.0	155.5	0.227
g, -Br	72.0	154.0	0.232
h, -I	72.0	154.0	0.18
i, -NO ₂	77.5	166.5	0.778

^a Chemical shifts are given in c.p.s. downfield from internal tetramethylsilane at 60 Mc. ^b Hammett *para*-substituent constants based on the ionization of substituted benzoic acids as reported by D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

To minimize solvent effects on the chemical shifts of the compounds under study the spectra were run as 5% (w./v.) solutions in carbon disulfide. Further dilution did not change the chemical shifts of the aliphatic protons within the experimental error of the measurements. It has been shown that solvent effects can markedly affect the chemical shifts of aromatic ring protons^{14,27} as well as the shift of the methyl group in substituted anisoles.²³

Within the experimental errors of measurement the coupling constants in the series of compounds Ia-e are unchanged in going from one compound to another; $J_{AX} = 4.2$, $J_{BX} = 8.9$, and $J_{AB} = -12.7$ c.p.s.

(26) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 132.

(27) T. Schaefer and W. G. Schneider, *J. Chem. Phys.*, **32**, 1218, 1224 (1960).

Discussion

In the series of bicyclic compounds IIa-f and the cyclopropanes IIIa-f the chemical shifts of the A, B, and X protons show wide, nonlinear variations in going from one member of a series to another. But, as has been shown previously,² the internal chemical shifts, $\delta_X - \delta_A$ and $\delta_X - \delta_B$, are linear functions of the electronegativity of the substituent. Furthermore the difference between these internal chemical shifts, $(\delta_X - \delta_A) - (\delta_X - \delta_B)$, is not constant, but seems to depend on the dihedral angle between the vicinal protons (as well as the electronegativity of the substituent). The purpose in studying the present series of compounds was to determine whether this same effect would be noted when a phenyl group was interposed between the substituent and the coupling proton. In this way one might separate the purely inductive effects of the substituent from the magnetic anisotropy of the substituent.

It is clear from a consideration of the data in Table I as presented graphically in Fig. 1a that the previously observed phenomena simply do not exist. It is seen

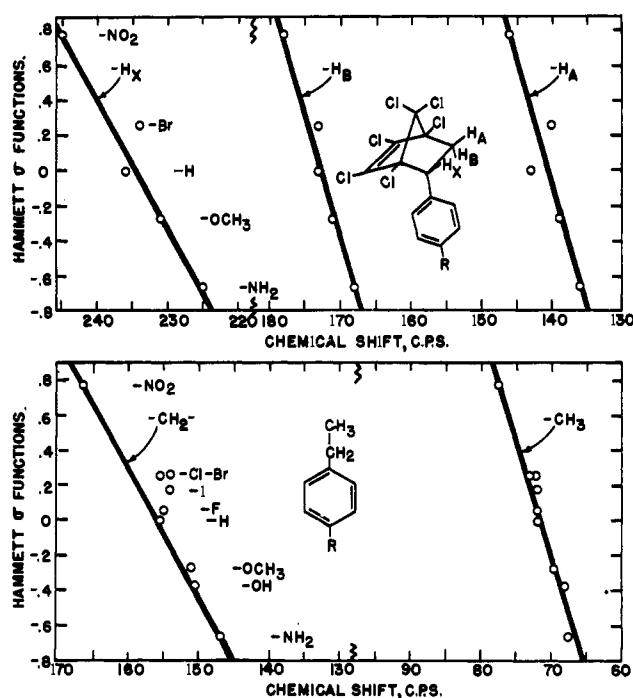


Fig. 1.—Chemical shifts vs. Hammett σ -constants for: (upper) the *para*-substituted phenylhexachlorobicyclo[2.2.1]heptenes and (lower) the ethylbenzenes.

that the internal chemical shifts $\delta_X - \delta_A$ and $\delta_X - \delta_B$ do not change from one member of the series to another. We would presume then that the effects that have been previously observed (in particular the angular dependence of the internal chemical shift) is due to the magnetic anisotropy of the various substituents acting upon the adjacent protons. We cannot rule out, however, the possibility that in the *para*-substituted phenyl bicyclic compounds the effect of the substituent is so greatly diminished because of the number of intervening bonds that it is not observed.

In Fig. 1a it is seen that the absolute value of the chemical shift of the X proton and of the A and B protons can be correlated with the Hammett σ_P -constant. Furthermore, the change in slope of these lines indi-

cates, as would be expected, that the effect of the substituent is decreased as the number of intervening bonds increases. A comparison with Fig. 1b where the chemical shifts of the methylene and methyl protons in the *para*-substituted ethylbenzenes are correlated with the σ -constants reveals that the *same* slopes are observed for the protons α and β to the phenyl group.²⁸ This indicates quite clearly that the ability of the substituent to donate and withdraw electrons from the α - and β -protons is the same in both the freely rotating ethylbenzenes and the rigid protons of the bicyclic system. Therefore the fact that the protons in the bicyclic system are rigidly fixed in relation to each other, are in a somewhat strained five-membered ring, and are adjacent to strongly electron-withdrawing centers makes no difference in the mobility of the electrons contributing to the relative shielding of the A, B, and X protons. In particular, as already noted, the substituent in the *para* position of the phenyl group has no more effect on proton A than on proton B—a fact that is not true when the substituent is attached directly to the bicyclic ring system. Of course the absolute values of the chemical shifts of the A, B, and X protons are affected by being a part of the halogenated bicyclic ring system—the effect being to displace all resonances to lower field relative to the ethylbenzenes. From the work of Fraser²⁹ on completely protonated bicycloheptenes, we can assume that about half (12–15 c.p.s.) of the chemical shift differences between the A and B protons is due to the anisotropy of the double bond between the 5- and 6-carbon atoms. The remainder is probably due to the anisotropy of the phenyl ring.

Experimental

The proton magnetic resonance spectra were obtained with a Varian Associates DP-60 high-resolution n.m.r. spectrometer operating at a frequency of 60 Mc./sec. Chemical shifts are reported in c.p.s. downfield from tetramethylsilane and are considered accurate to ± 0.015 p.p.m. Each sample was run on a 5% (w./v.) solution in carbon disulfide containing 1% tetramethylsilane as an internal standard. The chemical shifts were measured by the side-band technique; the frequency of the audiooscillator was measured with a Hewlett-Packard 521-C frequency counter. The line positions are the average of at least ten measurements.

The *para*-substituted ethylbenzenes were prepared by procedures previously described in the literature and physical properties for these compounds agreed closely with reported values.

5-Phenyl-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (Ic) was prepared according to the procedure of Polen, *et al.*,³⁰ by the Diels-Alder reaction of styrene with hexachlorocyclopentadiene. The product, after recrystallization from ethanol, had m.p. 72–73° (reported³⁰ 73.7–74.5°).

5-(*p*-Nitrophenyl)-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (Ie).—To 16.02 g. (0.0413 mole) of the styrene adduct I dissolved in 28 ml. of chloroform in a 250-ml. round-bottomed flask was added 64 ml. of concentrated sulfuric acid while maintaining the temperature at 5°. The reaction mixture was stirred vigorously with a magnetic stirrer while 2 ml. of fuming nitric acid was added dropwise over a period of 1 hr. The aqueous layer was discarded and the organic layer washed once with 10 ml. of water, once with 10 ml. of a 10% solution of sodium carbonate, and finally with 10 ml. of water. Upon removal of

(28) We cannot account for the deviation of the α -proton points from the correlation line when the substituent is one of the halogens. It is noteworthy that when *ortho* and *para* n.m.r. substituent constants are plotted *vs.* Hammett σ_p substituent constants for a series of *para*-disubstituted benzenes the halogens fall on a separate correlation line [G. W. Smith, *J. Mol. Spectry.*, **12**, 146 (1964)].

(29) R. R. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

(30) P. B. Polen, M. Kleiman, and H. G. Fechter, U. S. Patent 2,673,172, *Chem. Abstr.*, **48**, 8472 (1954).

the chloroform by distillation the residue spontaneously crystallized. Recrystallization from ethanol gave 10.15 g. (58.3% yield) of white crystals, m.p. 155–160°. A portion of this was recrystallized once more from ethanol to give material melting at 160–162° which was used for the n.m.r. spectrum. The reported³⁰ melting point is 159–160°.

An attempt to nitrate the styrene adduct according to the procedure of Polen, *et al.*,³⁰ gave only recovered starting material.

5-(*p*-Aminophenyl)-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (Ia) was prepared by the general procedure of Brown and Brown³¹ for the reduction of nitroaromatic compounds.

A 200-ml. three-necked round-bottomed flask containing a magnetic stirring bar was fitted with two small addition funnels through a Y-tube and a graduated buret. The third neck was connected to a gas absorption trap through a safety flask. In the reaction flask were placed 0.5 ml. of 0.2 *M* chloroplatinic acid, 20 ml. of ethanol, and 0.5 g. of activated charcoal. In one addition funnel was placed 4.22 g. (0.01 mole) of the nitro compound II, m.p. 160–162°, dissolved in 75 ml. of ethyl acetate. In the other addition funnel was placed 2 ml. of concentrated hydrochloric acid. In the graduated buret was placed a stabilized 0.99 *M* solution of sodium borohydride made by adding 3.7788 g. (0.099 mole) of sodium borohydride to 5 ml. of 10% sodium hydroxide solution and diluting to 100.0 ml. Over a period of 1 min. the catalyst was generated by introducing 2.4 ml. of the ethanolic solution of sodium borohydride to the vigorously stirred solution: the 2 ml. of hydrochloric acid was added slowly to destroy excess sodium borohydride and provide a hydrogen atmosphere; the reaction was then initiated by adding the nitro compound. The standard borohydride solution was added at such a rate that atmospheric pressure was maintained within the reaction flask. There was a sharp break in the curve of sodium borohydride added *vs.* time corresponding to the uptake of 97% of the theoretical amount of hydrogen. The reaction was stopped when gas absorption was essentially complete (about 0.5 hr.). The charcoal was removed by filtration, the filtrate made basic with 5% sodium hydroxide, and the product extracted with 100 ml. of ether. Evaporation of the ether left a clear oil which could not be induced to crystallize. Chromatography of a portion of this material on alumina and subsequent attempts at crystallization were also fruitless. A portion of the oil for analysis was evaporatively distilled at 0.2 mm.

Anal. Calcd. for C₁₃H₉Cl₆N: C, 39.81; H, 2.32; N, 3.57. Found: C, 40.02; H, 2.44; N, 3.57.

Polen, *et al.*, report the reduction of the nitro compound with iron powder and ferric chloride gives, in unspecified yield, the aniline as a solid, m.p. 105–106°. In our hands this procedure gave a 75% recovery of crystalline starting material. Similarly unsuccessful were attempts to reduce the nitro group with tin and hydrochloric acid as well as by hydrogenation in ethyl acetate using 10% palladium-on-carbon as the catalyst.

5-(*p*-Methoxyphenyl)-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (Ib) was prepared following the same procedure used to prepare the phenyl compound I.

In a 50-ml. round-bottomed flask equipped with a reflux condenser was placed 0.5 ml. (0.0037 mole) of *p*-methoxystyrene (Monomer-Polymer Laboratories) and 1.0 ml. (0.0037 mole) of hexachlorocyclopentadiene (Matheson Coleman and Bell). The mixture was heated at 165–170° in an oil bath for 2.5 hr., at which time there was no further evidence of refluxing. The red-brown liquid was cooled, taken up in hot ether, and cooled to deposit 0.6 g. of product as white prisms, m.p. 97–100°. Recrystallization once more from ethanol brought the melting point to 98.5–99.5°.

Anal. Calcd. for C₁₄H₁₀Cl₆O: C, 41.32; H, 2.48. Found: C, 41.37; H, 2.48.

5-(*p*-Bromophenyl)-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (Id).—Into a 150-ml. three-necked flask fitted with dropping funnel, reflux condenser, and gas absorption trap was placed 0.2 g. of iron filings and 4.10 g. (0.0105 mole) of the styrene adduct I, m.p. 72–73°, dissolved in 40 ml. of carbon tetrachloride. With magnetic stirring at room temperature a solution of 0.9 ml. (0.0165 mole) of bromine in 5 ml. of carbon tetrachloride was added dropwise. After 24 hr. of stirring, the reaction mixture was heated on the steam bath to vaporize unreacted bromine. The reaction mixture was diluted with water, ex-

(31) H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **84**, 1493 (1962); **84**, 2827 (1962).

tracted with ether, the ether layer washed several times with water, then the solvent dried and removed by distillation. The residue was taken up in hot ethanol and cooled to deposit 1.85 g. (38.2%) of brownish prisms, m.p. 125–130°. A portion of this material was decolorized with Norit and recrystallized twice from ethanol to give white prisms, m.p. 130–131.5°. This material was used for the n.m.r. spectrum.

Anal. Calcd. for $C_{13}H_{17}Cl_2Br$: C, 34.23; H, 1.55. Found: C, 34.34; H, 1.60.

The structure of the products, inferred from the method of synthesis, was confirmed by the n.m.r. spectrum. Each of the substituted phenyl compounds gave the characteristic four-line AB multiplet expected for *para*-substitution on the aromatic nucleus.

[CONTRIBUTION FROM THE MELLON INSTITUTE, PITTSBURGH, PENNSYLVANIA]

Nuclear Magnetic Resonance Spectra of Substituted Ethanes. II. *meso*- and *dl*-2,5-Diphenylhexanediol-2,5

BY D. JUNG AND A. A. BOTHNER-BY

RECEIVED APRIL 22, 1964

The high-resolution proton magnetic resonance spectra of the title compounds have been obtained and analyzed in terms of chemical shifts and coupling constants. Expressions for the coupling constants in terms of rotamer populations and characteristic *gauche* and *trans* coupling constants are given, and it is shown that the forms of these expressions confer some unique advantages upon compounds of this type, as subjects for the study of rotational isomerism about the central bond. ΔH for the *meso* compound is estimated at 1.1 kcal., that for the *dl*-compound as 1.4 kcal., with the *s-trans* arrangement of the bulky groups preferred over the *gauche* arrangement.

Introduction

Several studies^{1–6} have been made of the proton n.m.r. spectra of 1,2-disubstituted ethanes, both for the purpose of finding appropriate values for H,H-coupling constants between pairs of protons in the *trans* and *gauche* relations to each other, and with the idea of measuring relative populations of rotamers assuming reasonable values for these constants. In the typical case of a disubstituted ethane, XCH_2CH_2Y , the conformers are those shown in Fig. 1. The populations of the three forms are related: $p_2 = p_3 = (1 - p_1)/2$.

Since at most temperatures interconversion between the three rotamers is rapid, n.m.r. constants which are weighted averages of those in the three forms are observed. With the usual assumption¹ that in a given compound *gauche* and *trans* oriented protons are coupled by characteristic amounts, J_g and J_t , one may write

$$J_{AB} = J_{A'B'} = \frac{1 + p_1}{2} J_g + \frac{1 - p_1}{2} J_t \quad (1)$$

and

$$J_{AB'} = J_{A'B} = (1 - p_1)J_g + p_1J_t \quad (2)$$

whence

$$2J_{AB} + J_{AB'} = 2J_g + J_t \quad (3)$$

$$p_1 = (J_{AB'} - J_g)/(J_t - J_g) = (J_t + J_g - 2J_{AB})/(J_t - J_g) \quad (4)$$

Two difficulties frequently occur in the analysis of the data. First, if the values of J_{AB} and $J_{AB'}$ are nearly the same, the spectrum may display deceptive simplicity,^{1,4,7} and only the sum of the two constants is exactly determinable under these circumstances. Second, even if exact values for this pair of constants

can be obtained, the question of which value belongs to which constant remains. The assignment cannot be made from the spectrum.⁸ Equation 3 may be of help in discarding unreasonable values (since studies on the size of this sum have been made on ethyl derivatives and in other cases).^{1,9} If, for example, the pair of numbers (+6 c.p.s., +8 c.p.s.) were obtained for the two constants, then the two interpretations $J_g = +4$, $J_t = +12$, $p_1 = 0.5$, and $J_g = 4$, $J_t = 14$, $p_1 = 0.2$ would appear about equally attractive. Nor would lowering the temperature to increase the proportion of more stable rotamers be of any help: the same qualitative behavior would be observed whichever assignment were correct.

When a methylene group is adjacent to one carbon bearing three unlike substituents, the two protons of the methylene group are magnetically nonequivalent, and may display different chemical shifts.¹⁰ This suggests that 1,2-disubstituted ethanes, where the substituents are such asymmetric groups, might be suitable for studies aimed at determining the populations of rotamers about the central C-C single bond. Such compounds can exist in *meso*- and *dl*-forms. The rotamers are as shown in Fig. 2.

For the *meso* compound, where the *gauche* forms are of equal energy and population, one may write, with the same assumptions as for XCH_2CH_2Y compounds

$$J_{AA'} = J_{BB'} = (1 - p_1)J_g + p_1J_t \quad (5)$$

$$J_{AB} = J_{A'B'} = J_{gem} \quad (6)$$

$$J_{AB'} = J_{A'B} = \frac{1 + p_1}{2} J_g + \frac{1 - p_1}{2} J_t \quad (7)$$

$$J_{AA'} + 2J_{AB'} = 2J_g + J_t \quad (8)$$

$$p_1 = (J_{AA'} - J_g)/(J_t - J_g) = (J_t + J_g - 2J_{AB'})/(J_t - J_g) \quad (9)$$

- (1) R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, **9**, 165 (1963).
 (2) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **84**, 743 (1962).
 (3) F. A. L. Anet, *ibid.*, **84**, 747 (1962).
 (4) S. S. Danyluk, *Can. J. Chem.*, **41**, 387 (1963).
 (5) H. S. Gutowsky, *Pure Appl. Chem.*, **7**, 93 (1963); H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *J. Chem. Phys.*, **36**, 3353 (1962).
 (6) C. N. Banwell, A. D. Cohen, N. Sheppard, and J. J. Turner, *Proc. Chem. Soc.*, 266 (1959); N. Sheppard and J. J. Turner, *Proc. Roy. Soc. (London)*, **A262**, 506 (1959).
 (7) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

- (8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 142.

- (9) C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, **34**, 115 (1962).

- (10) P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957).