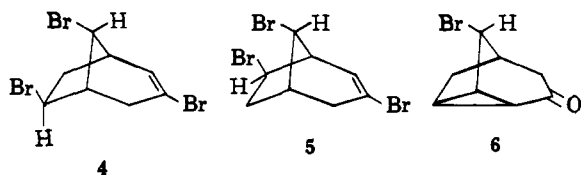


The dibromocarbene adduct of norbornadiene was reduced with lithium aluminum hydride to pure 3-bromobicyclo[3.2.1]octa-2,6-diene (**3**).¹ Bromination of **3** in ether at -10° afforded an 84% yield of a crystalline tribromide, m.p. $100-101^\circ$. *Anal.* Calcd. for $C_8H_9Br_3$: C, 27.85; H, 2.60; Br, 69.51. Found: C, 27.62; H, 2.60; Br, 69.39. Several possibilities were available for the structure of the tribromide; however, the spectral data are consistent with either 3,6,8- (**4**) or 3,7,8-tribromobicyclo[3.2.1]oct-2-ene (**5**). Pertinent n.m.r. data are δ 6.14 (1 H), 2 doublets, $J_1 \sim 7.4$ c.p.s., $J_2 \sim 2.0$ c.p.s. (C-2); δ 4.45 (1 H), singlet (*syn*-C-8); δ 4.35 (1 H), triplet, $J \sim 5.0$ c.p.s. (*endo*-C-6 or C-7); and a complex pattern between δ 3.16 and 2.26 (6 H).



Hydrolysis of the tribromide in aqueous ethanol containing sulfuric acid at 50° led to the bromoketone **6** (56%), m.p. $56.5-57.8^\circ$. *Anal.* Calcd. for C_8H_9OBr : C, 47.78; H, 4.51; Br, 39.75. Found: C, 47.81; H, 4.53; Br, 39.47. The n.m.r. spectrum showed a singlet (1 H) at δ 4.34; complex patterns at $\delta \sim 1.74$ (2H), 2.05 (2H), and 2.38 (4H). The infrared spectrum showed $\nu_{\max}^{CHCl_3}$ 1720 cm^{-1} . Structure **6** is best accommodated by these data.

When the bromoketone **6** was treated with potassium *t*-butoxide, an excellent yield of a halogen-free ketone, m.p. $69.5-70.5^\circ$, was obtained. *Anal.* Calcd. for C_8H_8O : C, 79.97; H, 6.71. Found: C, 79.76; H, 6.93. The dinitrophenylhydrazone derivative melted at $225-226^\circ$ (dec.). *Anal.* Calcd. for $C_{14}H_{13}N_4O_4$: C, 56.00; H, 4.03; N, 18.66. Found: C, 56.06; H, 4.28; N, 18.46. The ketone was assigned the structure **1** on the basis of its spectral properties: $\nu_{\max}^{CCl_4}$ 1720 cm^{-1} ; λ_{\max}^{EtOH} 281, 205 $m\mu$ (ϵ 50, 5360); n.m.r. complex pattern between δ 1.3 and 2.6. Unambiguous evidence for structure **1** is given by the mass spectrum² (Fig. 1) which confirmed the molecular formula. Of equal significance is the remarkable similarity of the mass spectrum of quadricyclene³ and other C_7H_8 isomers.⁴ Since a primary process of decomposition of **1** upon electron impact would be expected to be the loss of carbon monoxide, this correspondence was not unexpected.

The ketone **1** showed no exchange of deuterium (mass spectrum) when heated with sodium ethoxide and deuterioethanol. Cleavage with sodium amide in dioxane afforded all *cis*-3-carboxamidotricyclo[4.1.0.-0^{2.4}]heptane (**7**), with m.p. $209-210^\circ$, ν_{\max} 1680, 1590

(1) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963). We wish to thank Prof. Moore for informing us of these procedures prior to publication.

(2) The spectrum was obtained with a CEC 21-103C mass spectrometer, stainless-steel inlet system operated at 170° , ionization potential 70 e.v., ionization current 50 μ a., temperature of ion source 250° . We are indebted to Prof. D. C. DeJongh for the determination and to Prof. K. Biemann for the use of the spectrometer. A preliminary mass spectrum was obtained through the courtesy of Prof. K. L. Rinehart and Dr. T. H. Kinstle, University of Illinois, with an Atlas CH/4 spectrometer.

(3) Z. Dolejssek, V. Hanus, and H. Prinzbach, *Angew. Chem. Intern. Ed. Engl.*, **1**, 598 (1962).

(4) S. Meyerson, *J. Am. Chem. Soc.*, **85**, 3340 (1963).

cm^{-1} . *Anal.* Calcd. for $C_8H_{11}NO$: C, 70.04; H, 8.04; N, 10.21. Found: C, 70.01; H, 8.24; N, 10.45. Reduction of **1** with sodium borohydride in methanol afforded a mixture of two alcohols (**8** and **9**), m.p. $82-85^\circ$, in the ratio 80:20 as determined by gas chromatography. Oxidation of the mixture with chromic acid regenerated the starting ketone. On the assumption that the bottom side of **1** is least hindered, the major component of the alcohol mixture is considered to be the *exo* isomer **8**.

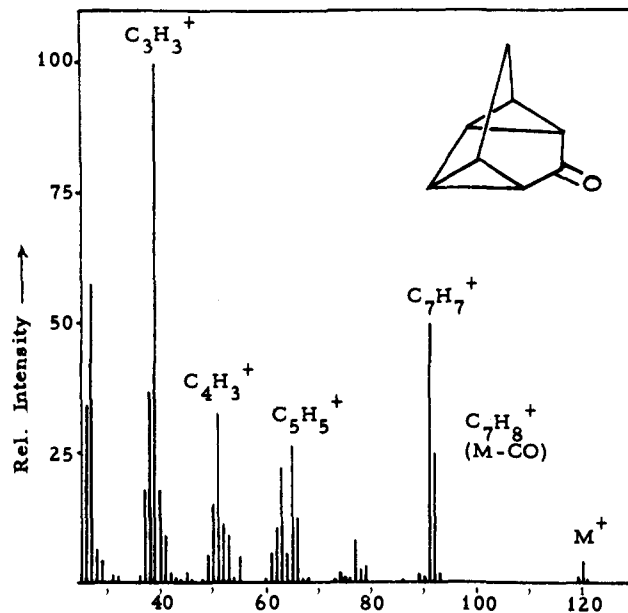
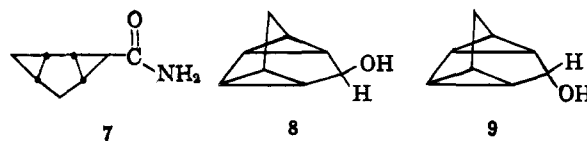


Figure 1.

An n.m.r. spectrum of **1** was taken in concentrated H_2SO_4 , from which solution dilution with water allowed 35% recovery of ketone. A noticeable simplification of the spectrum took place, but conclusions regarding



the significance of the observation must await further data.⁵

Acknowledgment.—This work was supported by the Alfred P. Sloan Foundation.

(5) NOTE ADDED IN PROOF.—The homologous tetracyclic ketone, quadriclanone, has recently been reported: P. R. Story and S. R. Fahrenholtz, *J. Am. Chem. Soc.*, **86**, 1270 (1964). Compound **1** is also quite polar, and its measured dipole moment in benzene at 25° ($\mu = 3.74$ D.) is unusually large.

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The Proton Magnetic Resonance Spectra and Rotational Barriers of 4,4'-Disubstituted Biphenyls¹

Sir:

We present in this communication results of a study of the proton magnetic resonance spectra of 4,4'-

(1) Supported by National Science Foundation Grant G11279. Abstracted in part from a thesis submitted by W. B. Wise in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology, Pittsburgh, Pa., Jan., 1964.

disubstituted biphenyls.² Our investigation is concerned with two questions: the first, the relation of the average dihedral angle to the chemical shift between the *ortho* and *meta* protons; the second, the determination of the potential curve for hindered rotation about the interannular bond from the temperature variation of this chemical shift.³

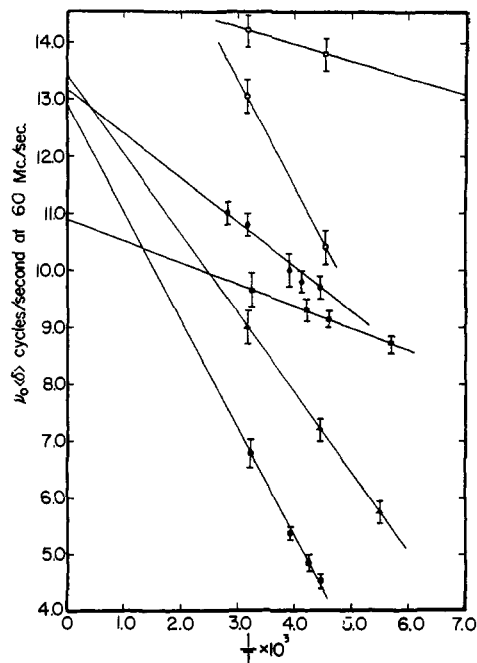


Fig. 1.—Biphenyl-4,4'- d_2 in: \blacklozenge , methylcyclohexane; \blacksquare , methylene chloride; \blacktriangle , chloroform-carbon tetrachloride; \bullet , carbon disulfide. 4,4'-Dimethylbiphenyl in: \square , methylene chloride; \circ , carbon disulfide.

The observed chemical shift between *ortho* and *meta* protons may be expanded in a Fourier series in $\langle \cos 2n\alpha \rangle$, where α is the dihedral angle, and where an average of $\cos 2n\alpha$ has been taken over all torsional states. The ring-current shift tables of Johnson and Bovey⁴ may be used to evaluate the first few terms in the series for assumed structural parameters (taken from electron diffraction studies on biphenyl in the gas phase⁵).

$$\nu_0(\delta) = 9.42 + 14.18\langle \cos 2\alpha \rangle - 0.90\langle \cos 4\alpha \rangle - 0.02\langle \cos 6\alpha \rangle \quad (1)$$

In eq. 1, $\nu_0(\delta)$ is expressed in cycles per second at a magnetic field strength corresponding to 60 Mc.p.s.⁶ $\langle \cos 2n\alpha \rangle$ is assumed to be given by

$$\langle \cos 2n\alpha \rangle = \int_0^{\pi/2} \exp[-V(\alpha)/RT] \cos 2n\alpha d\alpha / \int_0^{\pi/2} \exp[-V(\alpha)/RT] d\alpha \quad (2)$$

(2) A portion of the work described herein, *viz.*, that dealing with the room temperature proton n.m.r. spectra of biphenyl-4,4'- d_2 and the other 4,4'-disubstituted biphenyls, was presented at the Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, Ohio, June, 1963.

(3) Hoffman, *et al.* [Arkiv Kemi, **15**, 533 (1960)], have pointed out that the ring current shift [J. A. Pople, *J. Chem. Phys.*, **34**, 1111 (1956)] between *ortho* and *meta* protons in biphenyl should be correlated with the dihedral angle between the rings. However, Hoffman, *et al.*, using the theory of spectral moments, were not successful in unambiguously determining this shift from the n.m.r. spectrum of biphenyl itself.

(4) C. E. Johnson and F. A. Bovey, *ibid.*, **29**, 1012 (1958).

(5) O. Bastiansen, *Acta Chem. Scand.*, **3**, 408 (1949).

(6) A positive value for $\nu_0(\delta)$ implies that the signal arising from the *meta* protons appears at higher field than that arising from the *ortho* protons.

where $V(\alpha)$ is the potential curve for rotation about the interannular bond, R is the gas constant, and T is the absolute temperature. If a potential curve of the form $V(\alpha) = V_0 + (V_2/2)(1 + \cos 2\alpha) + (V_4/2)(1 + \cos 4\alpha)$ is assumed, then we have

$$\langle \cos 2\alpha \rangle = -\frac{\partial}{\partial x} [\ln I(x,y)] \quad (3a)$$

$$\langle \cos 4\alpha \rangle = -\frac{\partial}{\partial y} [\ln I(x,y)] \quad (3b)$$

where x is $V_2/2RT$, y is $V_4/2RT$, and

$$I(x,y) = \pi I_0(x)I_0(y) + 2\pi \sum_{m=1}^{\infty} [(-1)^m I_{2m}(x)I_m(y)] \quad (3c)$$

with $I_{2m}(x)$ and $I_m(y)$ modified Bessel functions of order $2m$ and m , having arguments x and y , respectively.⁷

Spectra were obtained on a Varian Associates DP-60 spectrometer at 60 Mc.p.s.⁸ Frequencies were measured with respect to tetramethylsilane or cyclohexane as internal reference using standard side-band interpolation techniques. All spectra of the A_2B_2 type were analyzed using the methods developed by Dischler and Maier.⁹ The spectrum of 4,4'-difluorobiphenyl was treated as an ABX spectrum and analyzed with the help of formulas given by Pople, *et al.*¹⁰

The results obtained for the various 4,4'-disubstituted biphenyls are presented in Table I. For comparison, also presented in Table I are the chemical shifts calculated by use of the substituent corrections given by Spiesscke and Schneider¹¹ for monosubstituted benzenes and with a ring-current correction corresponding to $\langle \cos 2\alpha \rangle$ set equal to zero in eq. 1. In Fig. 1 are presented $\nu_0(\delta)$ vs. $1/T$ of biphenyl-4,4'- d_2 in the solvent systems carbon disulfide, equivolume mixture of chloroform- d and carbon tetrachloride, methylcyclohexane, and methylene chloride, and $\nu_0(\delta)$ for 4,4'-dimethylbiphenyl in carbon disulfide and methylene chloride.¹²

The calculated chemical shifts in Table I are in approximate agreement with the experimentally derived values. However, the chemical shift extrapolated to infinite temperature (*i.e.*, $1/T = 0$) is about 13.2 c.p.s. for biphenyl-4,4'- d_2 in the solvents methylcyclohexane, chloroform-carbon tetrachloride, and carbon disulfide.¹³ We therefore take the constant term to be 13.2 c.p.s.

It is not obvious whether the solvent affects the temperature variation of $\nu_0(\delta)$ by altering the

(7) H. B. Dwight, "Tables of Integrals and other Mathematical Data," The Macmillan Company, New York, N. Y., 1960, p. 181.

(8) The spectra of biphenyl-4,4'- d_2 were obtained while deuterium nuclei were simultaneously irradiated at ca. 9.209 Mc.p.s. The spin decoupler was obtained from NMR Specialties, Inc., New Kensington, Pa.

(9) B. Dischler and W. Maier, *Z. Naturforsch.*, **16a**, 318 (1961).

(10) 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.

(11) H. Spiesscke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961).

(12) The temperature variation of the chemical shift $\nu_0(\delta)$ for biphenyl-4,4'- d_2 in acetone and acetonitrile was less than 0.2 c.p.s. (at 60 Mc.p.s.) over a temperature range of ca. 40 to -50° .

(13) It is reasonable that a small substituent effect, independent of average dihedral angle, and in addition to the ring current effect, be attributed to the phenyl ring; corresponding to such a substituent effect, a small chemical shift (ca. 1 p.p.m.) has been observed between *ortho* and *meta* carbons in the C^{13} n.m.r. spectrum of biphenyl by Friedel and Retcofsky (personal communication).

rotational barrier¹⁴ or by causing temperature-dependent differential chemical shifts of the sort discussed by Buckingham, *et al.*¹⁵

However, for aromatic compounds in which internal rotation is absent or strongly hindered, the variation of the chemical shift with temperature is much smaller than that of biphenyl-4,4'-*d*₂ or 4,4'-dimethylbiphenyl, the solvent being carbon disulfide in all these cases.¹⁶

TABLE I

Solvent	Substituent	Concentration, mg./ml.	$\nu_0(\delta)$, c.p.s. at 60 Mc.p.s.	
			Obsd.	Calcd.
C ₆ H ₁₂	D	200	10.5	10.3
C ₆ H ₁₁ CH ₃	D	33	10.8	10.3
CH ₂ Cl ₂	D	33	9.3	10.3
(CHCl ₂) ₂	D	200	9.3	10.3
Diglyme	D	200	9.1	10.3
(CH ₃) ₂ CO	D	33	10.8	10.3
CH ₃ CN	D	33	10.7	10.3
CS ₂	D	33	7.2	10.3
CH ₂ Cl ₂	CH ₃	13	14.2	
CS ₂	CH ₃	13	12.8	
(CHCl ₂) ₂	F	200	21.5	27.6
C ₆ H ₆	Cl		10.0 ^a	7.2
CH ₂ Cl ₂	Cl		6 ^a	7.2
(CHCl ₂) ₂	Cl	200	>3.8 <i>ca.</i>	7.2
Diglyme	Cl	200	8.9	7.2
(CHCl ₂) ₂	Br	200	9.2	8.4
Diglyme	Br	200	>3.8 <i>ca.</i>	8.4
(CHCl ₂) ₂	I	200	29.9	28.8
(CHCl ₂) ₂	NO ₂	200	32.4	34.2
Diglyme	NO ₂	200	22.9	34.2

^a D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 470 (1963).

Equations 3a and 3b may be expanded to third order in x and y and fitted by least squares to the observed temperature variation of $\nu_0(\delta)$. Values obtained for V_2 are $4.4 \pm 0.5 \times 10^2$ cal./mole, $7 \pm 1 \times 10^2$ cal./mole, and $11.0 \pm 2.5 \times 10^2$ cal./mole for biphenyl in methylcyclohexane, chloroform-carbon tetrachloride, and carbon disulfide, respectively, and limits for V_4 of ± 100 cal./mole. These values are consistent with a potential barrier which is relatively small and which has a minimum close to a dihedral angle of $\pi/2$.¹⁷

(14) A. K. Colter and L. C. Clemens have found solvent effects in the racemization rate of 1,1'-binaphthyl [*J. Phys. Chem.*, **68**, 651 (1964)].

(15) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **38**, 1227 (1960).

(16) The aromatic line positions of the following compounds show no change (to within experimental error, ± 0.2 to ± 0.4 c.p.s., depending on line width) over the indicated temperature range: toluene, *o*-xylene, *m*-xylene, *p*-xylene (38 to -86°), phenanthrene (33 to -56°), 4,6-dimethyl-dibenzothiophene (-31 to 36°). For 2-methylbiphenyl and 2,2'-dimethylbiphenyl-4,4'-*d*₂, the changes in differential (*ortho-meta*) chemical shift are *ca.* 1.8 ± 0.8 c.p.s. and 1.8 to 2.5 c.p.s., respectively, over the temperature range 44 to -90° ; the extrapolated change for biphenyl-4,4'-*d*₂ over this same range is 4.0 c.p.s.

(17) F. Adrian [*J. Chem. Phys.*, **26**, 608 (1958)] and I. Fischer-Hjalmars [*Tetrahedron*, **19**, 1805 (1963)] have both calculated potential energy curves which possess shallow minima at about 40° rather than 90° , agreeing with the electron diffraction results of ref. 4.

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Study of Isopolymolybdates in Aqueous Solution with the Aid of the Quinhydrone Electrode

Sir:

The quinhydrone electrode and its salt error have been studied, after Biilmann,¹ mainly by American

authors such as Cullen,² Morgan, Lammert, and Campbell,³ Corran and Lewis,⁴ La Mer and Baker,⁵ Hovorka and Dearing,⁶ Gabbard,⁷ Harned and Wright,⁸ and Hayes and Lietzke.⁹ We feel it, therefore, worthwhile to present in *J. Am. Chem. Soc.* a brief summary of the main conclusions we were led to, while studying the formation of isopolymolybdates with the aid of the quinhydrone electrode.

(1) If we define the salt error of the quinhydrone electrode as $\Delta E = -RT/2F \ln f_h/f_q$ (f_h and f_q being the activity factors of hydroquinone and quinone, respectively), we conclude, in opposition with the results obtained by Gabbard,⁷ that, in a given salt solution, for instance 3 *M* NaCl, the salt error ΔE is independent of the pH. This has been proved between pH 1.00 and 8.25, for well buffered solutions, by measuring the e.m.f. of the cell

Pt; H₂ (1 atm.), buffer + NaCl (3 *M*), quinhydrone; Au

whose constant value (after correction for the small salt error due to the buffer) was found to be 0.69140 abs. v. ± 0.2 mv. at 25° .

(2) We have shown that in poorly buffered mediums the "acidifying effect ΔpH " due to the ionization of hydroquinone is given by

$$\log \Delta pH = \log dpH/dx + \log S/C + pH - pK'$$

with the following notations: the pH is that of the solution under test, the pK' is that of hydroquinone (considered in a first approximation as a weak monobasic acid) in the given salt solution, and S is the concentration of hydroquinone (equal to the solubility of quinhydrone) in the given medium. C is the concentration of the buffer and dpH/dx the reciprocal of the buffer capacity.

(3) The standard potential of the quinhydrone electrode was found to be 0.69972 abs. v. ± 0.03 mv. at 25° .

(4) A receipt for recrystallization of quinhydrone has been indicated, and a method to verify its stoichiometry with an accuracy of 0.02% has been described.

(5) Different distributing effects on the potential of the quinhydrone electrode have been studied, *e.g.*, reaction with glycine buffer, oxidation through molybdates, and drifting of quinone vapors by inert gases like nitrogen or argon.

(6) Recrystallization of NaCl has been described; to avoid the formation of traces of NaOH, wet recrystallized NaCl must be dried at a temperature not higher than 45° .

(7) The study of the molybdates was made by means of progressive displacement of the molybdic acid from Na₂MoO₄ solutions, with HCl, and measuring the pH. All solutions were 3 *M* in respect to NaCl and the concentration of Na₂MoO₄ varied from $M/2$ to $M/3200$.

The interpretation was made with the Bye, Souchay, and Lefebvre¹⁰ method of the "potentiometric surface."

- (1) E. Biilmann, *Ann. Chim. (Paris)*, **15**, 109 (1921).
- (2) G. E. Cullen, *J. Biol. Chem.*, **85**, 535 (1929).
- (3) J. L. R. Morgan, D. M. Lammert, and M. A. Campbell, *J. Am. Chem. Soc.*, **53**, 454 (1931).
- (4) J. W. Corran and W. C. Mac. Lewis, *Biochem. J.*, **18**, 1358 (1924).
- (5) V. K. La Mer and L. E. Baker, *J. Am. Chem. Soc.*, **44**, 1954 (1922).
- (6) F. Hovorka and W. C. Dearing, *ibid.*, **57**, 446 (1935).
- (7) J. L. Gabbard, *ibid.*, **69**, 533 (1947).
- (8) H. S. Harned and D. D. Wright, *ibid.*, **55**, 4849 (1933).
- (9) J. C. Hayes and M. H. Lietzke, *J. Phys. Chem.*, **64**, 374 (1960).
- (10) J. Lefebvre, *J. Chim. Phys.*, **54**, 553 (1957).