Organic and Biological Chemistry

Diamagnetic Susceptibility Exaltation in Hydrocarbons

Hyp J. Dauben, Jr.,[1] James D. Wilson,[2,3] and John L. Laity

Contribution from the Department of Chemistry, University of Washington, Seattle, Washington 98105. *Received October 1, 1968*

Abstract: Diamagnetic susceptibility exaltation, defined as the difference between the measured molar susceptibility and the susceptibility estimated neglecting the contribution of ring current, is found to be a property solely of aromatic compounds by calculating the exaltations of a wide variety of aromatic and nonaromatic hydrocarbons. Nonbenzenoid *aromatic* compounds exhibit exaltation, pseudoaromatic compounds do not. Exaltation is proportional to the theoretically calculated "London diamagnetism" of aromatic compounds.

Despite more than 30 years of strong interest in the nature and limits of aromaticity, there has never been developed a completely satisfactory physical test for the presence of aromatic character in the many novel systems synthesized to test the predictions of theory in this field. This paper examines a phenomenon, exaltation of diamagnetic susceptibility, which provides just such a test.

In the course of his pioneering work on the magnetic properties of organic compounds, Pascal observed[4] that benzene and its derivatives exhibited somewhat larger susceptibilities than would be predicted for them from the susceptibilities of other unsaturated compounds. Pacault handled this discrepancy in the "Pascal System" for estimating susceptibilities by introducing[5] a special benzene-ring parameter called the "exaltation." Pink and Ubbelohde recognized[6] that the existence of exaltation could be used to identify aromatic compounds; they hypothesized that if measured and estimated susceptibilities were compared, exaltations would be found only for aromatic compounds. Unfortunately, this hypothesis could not be adequately tested because the original Pascal System, then in use, is relatively inaccurate,[7] and insufficient magnetic susceptibility data were available. The recent development[7,8] of more accurate systems for the estimation of diamagnetic susceptibility has cleared away the first of these difficulties. We have now obtained the data on crucial model compounds necessary to test the hypothesis, and present here in detail[9] the results which demonstrate its validity.

Results and Discussion

The diamagnetic susceptibility exaltation, Λ, is defined[5]

$$\Lambda = \chi_{M} - \chi_{M'} \qquad (1)$$

where χ_M is the experimentally determined molar susceptibility of a compound and $\chi_{M'}$ is the susceptibility estimated for a cyclopolyene of that structure, *i.e.*, omitting any "correction" for ring current. In this work values of χ_M not obtained from the literature were measured by one of two nmr methods[10–12] with accuracy and precision generally comparable to those of previously published values. Values of $\chi_{M'}$ were obtained using the magnetic susceptibility increment system of Haberditzl.[7,13] It should be noted here that these increment values contain a contribution from the Van Vleck paramagnetism[14,15] appropriate to molecules which are roughly disk shaped. Since the magnitude of the Van Vleck paramagnetism exhibited by a molecule depends on its shape,[15] it follows *that this set of increment values will predict accurately the susceptibilities of disk-shaped molecules only.* Generally, small variations in the shape will not cause large errors in the estimation of $\chi_{M'}$, but the susceptibilities of more nearly spherical molecules will be slightly underestimated[15,16] and those of long, flat molecules will be slightly overestimated.[15] An "annelation" increment, $A = 20.3$, applied to naphthalene, anthracene, phen-

---

(1) Died April 3, 1968.

(2) Author to whom inquiries should be addressed at Monsanto Co., Central Research Department, St. Louis, Mo. 63166.

(3) National Science Foundation Fellow, 1962–1966.

(4) For a review of Pascal's work see P. W. Selwood, "Magnetochemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1956, p 41.

(5) A. Pacault, *Ann. Chim., Ser. XII*, **1**, 567 (1946).

(6) R. C. Pink and A. R. Ubbelohde, *Trans. Faraday Soc.*, **44**, 708 (1948). See also D. Craig in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, New York, N. Y., 1959, pp 1–42.

(7) W. Haberditzl, *Sitzber. Deut. Akad. Wiss. Berlin, Kl. Chem. Geol. Biol.*, No. 2 (1964); *Angew. Chem. Intern. Ed. Engl.*, **5**, 288 (1966).

(8) See A. Pacault, J. Hoarau, and A. Marchand, *Advan. Chem. Phys.*, **3**, 171 (1961).

(9) A preliminary communication has appeared: H. J. Dauben, Jr., J. D. Wilson, and J. L. Laity, *J. Am. Chem. Soc.*, **90**, 811 (1968).

(10) K. Frei and J. Bernstein, *J. Chem. Phys.*, **37**, 1891 (1962).

(11) L. N. Mulay and M. Haverbusch, *Rev. Sci. Instr.*, **35**, 756 (1964); L. N. Mulay and I. L. Mulay, *Anal. Chem.*, **36**, 404R (1964); **38**, 501R (1966).

(12) D. C. Douglass and A. Fratiello, *J. Chem. Phys.*, **39**, 3161 (1963); J. R. Zimmerman and M. R. Foster, *J. Phys. Chem.*, **61**, 282 (1957).

(13) In connection with a systematic study (J. L. Laity and H. J. Dauben, unpublished work) of the susceptibilities of polyalkyl benzenes, we have found that both the Haberditzl[7] and revised Pascal[8] increment systems to be slightly (∼1%) inaccurate. From a computer-aided least-squares treatment of reliable susceptibility data we have obtained a new, more accurate set of susceptibility increments, which will be reported in detail elsewhere. However, the Haberditzl system is certainly accurate enough for the purposes of this present work.

(14) Reference 4, pp 83–85.

(15) Ya. G. Dorfman "Diamagnetism and the Chemical Bond," American Elsevier Publishing Co., Inc., New York, N. Y., 1965.

(16) Thus Haberditzl[7] found it necessary to adopt a set of increment values to predict susceptibilities of "adamantane-type" molecules different from the set used for open-chain molecules, because these seriously underestimated the values found for the nearly spherical molecules.

Table I. Diamagnetic Exaltation Data[a]

Compound	χ_M	$\chi_{M'}$	Λ
Nonaromatic Compounds			
Cyclopentane	59.2^b	56.8	2.4
Cyclopentene	49.5 ± 0.5^k	47.0	2.5
Cyclopentadiene (**1**)	$44.5^{b,k}$	38.0	6.5
5,5-Dimethylcyclopentadiene (**2**)	67.5 ± 0.6^k	62.7	4.8
Cyclohexane	68.1^b	68.1	0.0
Cyclohexene	57.5^b	58.3	−0.8
1,3-Cyclohexadiene	48.6^b	49.3	−0.7
1,4-Cyclohexadiene	48.7^b	48.5	0.2
Cycloheptane	78.9 ± 0.7^k	79.5	−0.6
Cycloheptene	69.3 ± 0.6^k	69.7	−0.4
1,3-Cycloheptadiene	61.0 ± 0.6^k	60.7	0.3
1,4-Cycloheptadiene	61.0 ± 0.4^k	59.9	1.1
1,3,5-Cycloheptatriene	59.8 ± 1.0^k	51.7	8.1
3,7,7-Trimethyl-1,3,5-cycloheptatriene	95.6 ± 0.4^k	88.5	7.1
7,7′-Bis(cycloheptatrienyl)	119 ± 3^k	100.0	19.0
Cyclooctane	91.4^b	90.8	0.6
Cyclooctene	80.5 ± 0.6^k	81.0	−0.5
1,3-Cyclooctadiene	72.8 ± 0.8^k	72.0	0.8
1,5-Cyclooctadiene	71.5 ± 0.7^k	71.2	0.3
1,3,5-Cyclooctatriene	65.1 ± 0.8^k	64.0	1.1
Cyclooctatetraene	$53.9^{i,k}$	54.8	−0.9
Cyclododecene	127 ± 1^k	126.4	0.6
Benzenoid Aromatic Compounds			
Benzene	54.8^b	41.1	13.7
Toluene	66.1^b	53.3	12.8
Styrene	68.2^b	55.6	12.6
Indene	$80.5^{b,k}$	61.4	19.1
Fluorene	110.5^c	84.8	25.7
Triphenylmethane	166^e	125	41
Stilbene	120^e	82	28
1,4-Diphenylbutadiene	130^e	106	24
Biphenyl	103.3^c	77.1	26.2
p-Diphenylbenzene	152^c	113	39
4,4′-Diphenylbiphenyl	201^c	149	52
Biphenylene (3)	88 ± 3^k	74	14
Naphthalene	91.9^b	61.4	30.5
Anthracene	130.3^b	81.7	48.6
Benzenoid Aromatic Compounds (*Continued*)			
Phenanthrene	127.9^b	81.7	48.6
Tetracene (**4**)	168^b	102	66
Chrysene (**5**)	167^b	102	65
Pentacene (6)	205^b	122	83
Dibenz[*a,h*]anthracene (**7**)	193^d	122	71
Fluoranthene (**8**)	138^c	96	42
Pyrene (**9**)	155^c	98	57
Triphenylene (**10**)	157^c	107	50
Perylene (**11**)	171^f	121	50
Benzo[*a*]pyrene (**12**)	194^b	119	75
Coronene (**13**)	243^b	140	103
Ovalene (**14**)	354^b	181	173
Nonbenzenoid Aromatic and Pseudoaromatic Compounds			
Azulene (**15**)	91.0^g	61.4	29.6
1,6-Methano[10]annulene (**16**)	111.9 ± 0.4^k	75.1	36.8
1,6-Oxido[10]annulene (**17**)	108.0 ± 0.5^k	69.1	38.9
trans-15,16-Dimethyl-15,16-dihydropyrene (**18**)	210 ± 15^k	129	81
1,3,6,8,15,16-Hexamethyl-15,16-dihydropyrene (**19**)	250 ± 20^k	178	72
Acepleiadylene (**20**)	155 ± 5^k	98	53
Dicyclopenta[*ef,kl*]heptalene (**21**)	151 ± 4^k	98	53
Acenaphthylene (**22**)	111.6^c	72.3	39.3
Acenaphthene (**23**)	109.3^b	82.4	26.9
Acepleiadiene (**24**)	135 ± 3^k	106	29
2-Phenyl-5,7-dimethylpleiapentalene (**25**)	179 ± 4^k	149^l	30
3,5-Dimethylaceheptalene (**26**)	112 ± 3^k	112	0.0
Pentafulvene (**27**)	43.0^h	41.9	1.1
Cyclooctatetraene (**28**)	$53.9^{i,k}$	54.8	−0.9
[16]Annulene (**29**)	105 ± 2^k	110	−5
Heptalene (**30**)	72 ± 7^k	78.2	−6
Heptafulvalene (**31**)	94 ± 3^k	92.0	2
9,10-Dimethyldibenzopentalene (**32**)	132^j	146^l	−14
7,7-Dimethylbenzofulvene	105^j	103^l	2
7-Phenylbenzofulvene	131^j	130^l	1

[a] All values of χ_M, $\chi_{M'}$, and Λ are given in units of -10^{-6} cm³ mol⁻¹. The values of $\chi_{M'}$ are not corrected for "ring-current diamagnetism." [b] G. W. Smith, "A Compilation of Diamagnetic Susceptibilities," General Motors Corporation Research Report, GMR-317, 1960. [c] G. W. Smith, "Supplement to GMR-317," GMR-396, 1963. [d] K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc.* (London), **A156**, 597 (1936). [e] K. S. Krishnan and S. Bannerjee, *Phil. Trans. Roy. Soc.* (London), **A234**, 265 (1935). [f] H. Shiba and G. Hazato, *Bull. Chem. Soc. Japan*, **22**, 92 (1949). [g] W. Klemm, *Ber.*, **90**, 1051 (1957). [h] J. Thiec and J. Weimann, *Bull. Soc. Chim. France*, 177 (1956). [i] S. Shida and S. Fujii, *Bull. Chem. Soc. Japan*, **24**, 173 (1951). [j] E. D. Bergmann, J. Hoarau, A. Pacault, B. Pullman, and A. Pullman, *J. Chim. Phys.*, **49**, 472 (1952). [k] This work. [l] Benzene-ring exaltation included.

anthrene, etc., and a "phenylation" increment, $P = 35.0$, applied to polyphenyls, have been introduced in an attempt to compensate for this second effect.[17,18]

The primary results of this work are the exaltations calculated as described above for a wide variety of aromatic and nonaromatic compounds. These are presented in Table I which contains data for nonaromatic, benzenoid aromatic, and nonbenzenoid aromatic and pseudoaromatic hydrocarbons. If the hypothesis above is correct and our method of estimating $\chi_{M'}$ is sufficiently accurate, we expect to find that all nonaromatic compounds will exhibit $\Lambda = 0$[19] and all aromatic compounds will exhibit $\Lambda > 0$.[20,21]

The first conclusion which emerges from the data of Table I is that the method used to obtain $\chi_{M'}$ appears to be accurate. Of all the "nonaromatic" compounds only six exhibit exaltations significantly different from zero, and all but one of these can be satisfactorily rationalized. By contrast, *all* the benzenoid aromatics exhibit substantial exaltations, as do the nonbenzenoid aromatics (**15–23**).[22] Taken together, these results convincingly demonstrate the validity of the hypothesis and show that *exhibition of diamagnetic susceptibility exaltation by a compound implies that it is an "aromatic" compound.* After examining the apparent exceptions to this found in Table I, we shall consider some of the consequences of the exaltations exhibited by some of the aromatic and pseudoaromatic compounds.

---

(17) Thus, for example, $\chi_{M'}(\text{naphthalene}) = \chi_{M'}(\text{benzene}) + A = 61.4$, and $\chi_{M'}(\text{biphenyl}) = \chi_{M'}(\text{benzene}) + P = 76.1$, both of which are less than the values obtained from the unmodified Haberditzl system.

(18) J. D. Wilson, Ph.D. Thesis, University of Washington, Seattle, Wash., 1966.

(19) Within the combined uncertainties of measurement of $\chi_{M'}$ about ±1%, and estimation of $\chi_{M'}$, also about ±1%. Thus values $|\Lambda| < 1$ are essentially zero and values $1 < |\Lambda| < 2$ must be skeptically considered and cautiously interpreted.

(20) Some compounds are found to exhibit $\Lambda < 0$; these are discussed below.

(21) Throughout this paper values of χ_M, $\chi_{M'}$, and Λ are given in units of -10^{-6} cm³ mol⁻¹.

(22) See Figure 1 for structures of some of the numbered compounds.

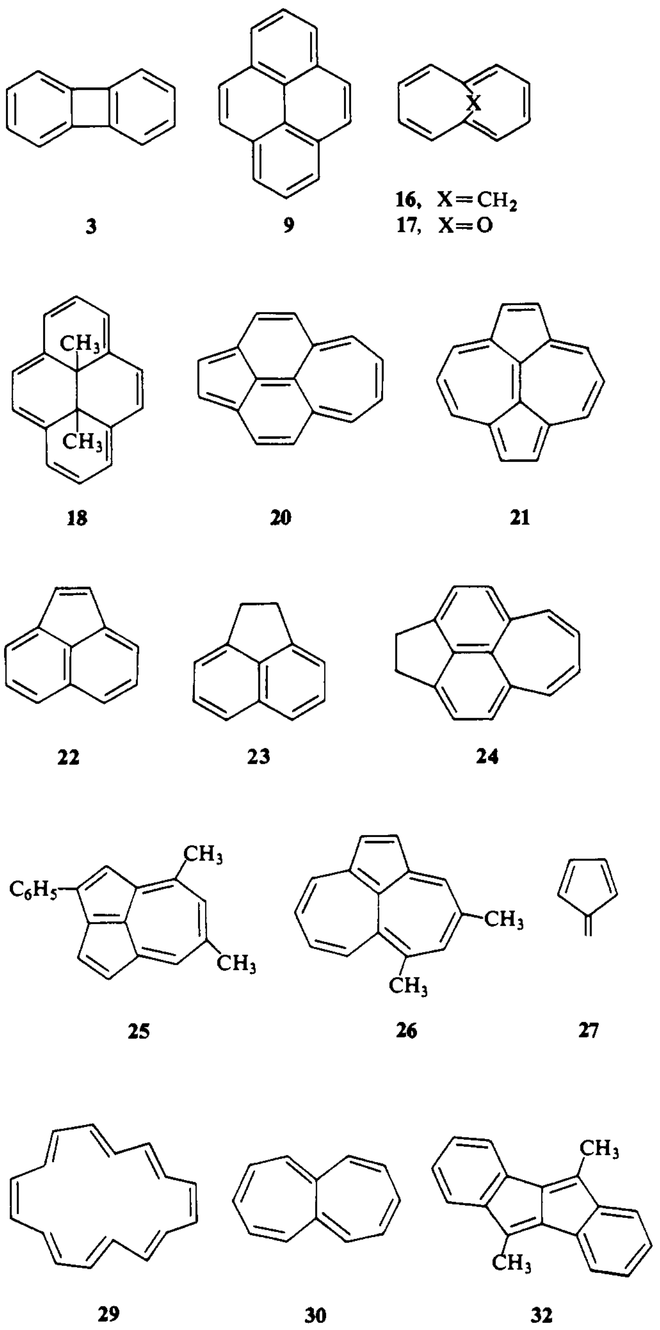

Figure 1. Structures of certain aromatic and pseudoaromatic compounds.

The existence of exaltation in cycloheptatriene and its derivatives is easily rationalized: these compounds possess aromatic character. This explanation has already been used to rationalize the resonance energy and certain features of the structure[23] of cycloheptatriene, and the value of the exaltation observed here is too large to be explained in any other way.

The small apparent exaltation exhibited by cyclopentane and cyclopentene undoubtedly arises from a failure of the method used to calculate $\chi_{M'}$. Not only are these systems not possibly aromatic, but cyclobutane and cyclopropane systems have been observed to exhibit similar, though more extreme, behavior.[24]

The deviation from normal behavior in these systems confuses results in the derivatives of cyclopentadiene. For most uses of the "susceptibility increment system" it would be sufficient to introduce a "five-membered ring" correction, to be applied when estimating the susceptibility of a cyclopentane derivative, but it is not obvious whether this correction should or should not be applied to cyclopentadienes and related systems. Were the "correction" applied to cyclopentadienes, the exaltation exhibited by **1** would become 4.0 and that of **2**, 2.3. The latter value is now almost small enough to be considered negligible, as would be predicted. If **2** does not really exhibit exaltation, it is doubtful that **1** should, since similarity of their nmr spectra[25] implies that they are electronically and magnetically very similar. However, the value $\Lambda = 4$ for cyclopentadiene is too large to be neglected offhand, and since it has been suggested[26] that **1** might exhibit cyclic delocalization *via* hyperconjugative σ–π overlap of the methylene-group C–H bonds with the π system, it is conceivable that the exaltation is real. In any case, this single anomaly does not appreciably weaken the case for exaltation as a valid test for aromaticity.

Nonbenzenoid Aromatic Compounds

Two kinds of nonbenzenoid aromatic compounds are represented by **15–21**, benzenoid isomers (azulene (**15**), acepleiadylene (**20**), and azupyrene[27] (**22**)) and bridged annulenes (1,6-methano- and 1,6-oxido[10]annulene (**16** and **17**) and the two 15,16-dihydropyrenes **18** and **19**). The exaltations of **15**, **20**, and **21** are virtually the same as their benzenoid isomers, naphthalene and pyrene, which implies that π systems on a lattice made up of equal numbers of five- and seven-membered rings are essentially equal to those on classical aromatic frameworks of six-membered carbocyclic rings.

Magnetic susceptibility data for the parent "Hückel" systems [10]- and [14]annulene would have been very desirable for this study but were not available.[28] Instead several derivatives of these compounds which retain their essential features were studied. Although [10]annulene (cyclodecapentaene) is known only as an unstable intermediate,[29] considerable evidence has been compiled to show that its 1,6-bridged derivatives **16** and **17** possess fully aromatic ground states.[30-32] The substantial exaltation exhibited by these compounds completely con-

---

(23) R. E. Davis and A. Tulinsky, *Tetrahedron Letters*, 839 (1962); M. Tratteborg, *J. Am. Chem. Soc.*, **86**, 4265 (1964).

(24) Thus cyclobutane exhibits $\Lambda = -1.5$ and cyclopropane, $+5.2$: J. L. Laity and H. J. Dauben, unpublished results.

(25) C. F. Wilcox, Jr., and M. Mesirov, *J. Org. Chem.*, **25**, 1841 (1960); G. V. Tiers, "NMR Summary," 3M Company, St. Paul, Minn., 1960.

(26) R. S. Mulliken, *J. Chem. Phys.*, **7**, 339 (1939); C. A. Coulson, "Valence," 2nd ed, Oxford University Press, London, 1961, p 312; G. W. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1955, pp 672–675.

(27) A. G. Anderson, Jr., A. A. MacDonald, and A. F. Montana, *J. Am. Chem. Soc.*, **90**, 2993 (1968).

(28) The magnetic *anisotropy* of bisdehydro[14]annulene has been measured [N. A. Bailey, M. Gerloch, and R. Mason, *Mol. Phys.*, **5**, 327 (1966)] but the *mean susceptibility* was not reported.

(29) E. E. van Tamelen and T. L. Burkoth, *J. Am. Chem. Soc.*, **89**, 157 (1967).

(30) E. Vogel in "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, pp 113–147.

(31) F. Sondheimer and A. Shani, *J. Am. Chem. Soc.*, **86**, 3168 (1964).

(32) M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **48**, 1429 (1965).

firms these findings. The slightly larger exaltation of **17** than **16** agrees with the downfield shift of 0.2 ppm in the respective nmr ring proton chemical shift values of the two compounds.[30] Apparently **17** bears the larger ring current. The aromatic nature of the *trans*-15,16-dimethyl-15,16-dihydropyrene ring systems has been established,[33,34] and this is again confirmed by the very large exaltations exhibited by **18** and **19**.

Naphthalene and azulene can be regarded as bridged [10]annulenes;[35] in this light it is instructive to compare the exaltations of these two compounds with those of **16** and **17**. The exaltations of the "simple" (*i.e.*, noncross-conjugated) derivatives of [10]annulene **16** and **17** are considerably the larger, *as has been predicted.*[35] Similarly, the exaltations of **18** and **19** exceed those of pyrene and its isomers which can be considered as ethylene-bridged [14]annulenes.

The question of aromatic character in biphenylene (**3**) has been the source of considerable study and dispute;[36] the exaltation exhibited by **3** establishes that this compound is undoubtedly aromatic. However, the magnitude of the exaltation is reduced compared to that of biphenyl ($\Lambda = 26.2$) or naphthalene (30.3). This probably reflects the combined effects of ring strain and the slight bond alternation[37] of the system, but it could also be interpreted as the result of partial cancellation of induced diamagnetic and paramagnetic ring currents.[38]

Acenaphthylene and Similar Systems

Considerable interest attends the class of tricyclic, peri-fused hydrocarbons of which acenaphthylene is the best known example, and four of these compounds provide an especially interesting test of this method. Two of these, acenaphthylene (**22**) and pleiapentalene (**25**, perhaps more accurately called "aceazulene"), are 12 π-electron systems, and the others, acepleiadiene (**24**) and aceheptalene (**26**, "pleaiazulene"), are 14 π-electron systems. All of these compounds exhibit chemical properties intermediate between those considered to be typically "aromatic" (*e.g.*, electrophilic substitution) and typically "olefinic" (*e.g.*, electrophilic addition).[39-41] In their nmr spectra, the ring-proton chemical shifts fall into the range intermediate between "aromatic" and "olefinic" protons.[18,39,41] From the exaltations which they exhibit, however, there can be no doubt that **22** and **25** are aromatic, that **24** is aromatic only in the naphthalene nucleus (compare the exaltations of **23** and **24**), and that **26** is not aromatic at all!

These results are not entirely anticipated by theory. Asgar-Ali and Coulson predicted[42] that **26** would be aromatic and **25** not, but Jung and Hafner[43] have recently completed calculations which agree with the above exaltations. Acenaphthylene was correctly predicted[44] to exhibit a larger exaltation than naphthalene, but the magnitude predicted is considerably larger than that found (*cf.* Table III). It is not obvious why theory has performed so poorly when applied to these systems, but it is clear that further work is indicated. The most puzzling observation to be explained is the complete absence of exaltation in **26**; naively, one would expect an azulene nucleus to show its existence and some exaltation to be found.

Pseudoaromatic Compounds

The last compounds listed in Table I are characterized as "pseudoaromatic;"[45] that is, they possess fully conjugated peripheries but none of the other electronic characteristics of aromatic compounds. These compounds are of particular interest to this study, for they have been extensively studied in order to determine the nature and limits of aromaticity. These compounds are found *not* to exhibit exaltation, a result which is perhaps not too surprising, considering that the majority of accumulated evidence supports the predictions that these compounds should be essentially polyenes. However, the data provide solid, unambiguous physical evidence that these "4*n*" systems can be considered in no wise aromatic.

It is of some current interest[46,47] that certain pseudoaromatic systems exhibit the phenomenon of *negative* exaltation, *i.e.*, at least three systems exhibit significant values of $\Lambda < 0$. This is quite apparent in the cases of [16]annulene ($\Lambda = -5$), heptalene (-6), and dimethyldibenzopentalene (**32**, -14).[48] These data add some support to the other theoretical and experimental evidence which have been found to support the existence of π-orbital paramagnetism in "4*n*" carbocyclic systems.[46,47,49] Measurement of the diamagnetic susceptibilities of other compounds of interest to this theory can now provide unambiguous data to test and refine the theory.

Note that the negative exaltations found here are relatively small in magnitude, probably too small, in fact, to allow the nmr behavior of systems such as [16]annulene to be rationalized on the basis of paramagnetic ring currents alone.[47b] This finding supports the hypothesis that these compounds exist largely as nonplanar, bond-alternant molecules. Further support for this can be seen in Table II, in which theoretically calculated values of the "ring current diamagnetism"[50] are compared with the

---

(33) V. Boekelheide and J. B. Phillips, *Proc. Natl. Acad. Sci. U. S.*, **51**, 550 (1964); *J. Am. Chem. Soc.*, **85**, 1545 (1963); **89**, 1695 (1967).

(34) A. W. Hanson, *Acta Cryst.*, **18**, 599 (1965).

(35) L. Salem, "Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966, Chapter 4, p 2.

(36) For reviews see W. Baker and J. F. W. McOmie in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, New York, N. Y., 1959, p 65; D. Lloyd, "Carbocyclic Non-Benzenoid Aromatic Compounds," Elsevier Publishing Co., Amsterdam, 1966, pp 45-51.

(37) T. C. W. Mak and J. Trotter, *Proc. Chem. Soc.*, 163 (1961); *J. Chem. Soc.*, 1 (1962).

(38) H. P. Figeys, *Chem. Commun.*, 495 (1967).

(39) K. Hafner and J. Schneider, *Angew. Chem.*, **70**, 702 (1958); *Ann.*, **624**, 37 (1959); K. Hafner and K. F. Bangert, *ibid.*, **650**, 98 (1961); K. Hafner and G. Schneider, *ibid.*, **672**, 194 (1964).

(40) V. Boekelheide, W. E. Langeland, and C.-T. Liu, *J. Am. Chem. Soc.*, **73**, 2432 (1951); V. Boekelheide and G. K. Vick, *ibid.*, **78**, 653 (1956).

(41) M. J. S. Dewar and R. C. Fahey, *ibid.*, **85**, 2245, 2704 (1963).

(42) M. Asgar-Ali and C. A. Coulson, *Mol. Phys.*, **4**, 65 (1961).

(43) D. Jung, personal communication.

(44) B. Pullman and A. Pullman, "Les Theories Electronique de la Chimie Organique," Masson et Cie., Paris, 1952, Chapter IX.

(45) D. P. Craig, *J. Chem. Soc.*, 3175 (1957).

(46) J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.*, **88**, 4811 (1966).

(47) (a) H. C. Longuet-Higgins, "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 109; (b) F. Baer, H. Kuhn, and W. Regel, *Z. Naturforsch.*, **22a**, 103 (1967).

(48) 9,10-Diphenyldibenzopentalene exhibits a negative exaltation of similar magnitude. Note that in calculating Λ in these cases, the value of χ_M' used *includes* the normal benzene-ring exaltation. Actually this should not be included in a proper calculation of Λ but it has been done here to emphasize the π-orbital paramagnetism of these systems.[49] With the benzene-ring exaltation *excluded*, the dibenzopentalene system exhibits $\Lambda = 14$.

(49) G. Wagniere and M. Gouterman, *Mol. Phys.*, **5**, 619 (1962).

Table II. Values of the Exaltation and "London Diamagnetism" of Pseudoaromatic Compounds

Compound	Λ/Λ(benzene)[a]	K_L/K_L (benzene) Bond equiv[b]	K_L/K_L (benzene) Bond altnt[c]
Pentafulvene	0.08	0.08	0.08
Heptafulvalene	0.15	...	0.12
Heptalene	−0.45	−8.34	−0.21
Cyclooctatetraene	0.00	...	0.0
Dibenzopentalene	+1.00[d]	−0.75	0.99

[a] Calculated from data of Table I. [b] B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson et Cie., Paris, 1952, p 545. [c] T. Nakajima, in "Molecular Orbitals in Chemistry, Physics, and Biology," P. O. Lowdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 451; T. Nakajima and S. Kohda, *Bull. Chem. Soc. Japan*, **39**, 804 (1966). [d] Exaltation of benzene rings excluded in calculation of $\chi_{M'}$.

value of Λ found in this work (for convenience both are expressed as ratios relative to the exaltation of benzene). The exaltations are seen to agree quite well with theoretical values of K_L calculated for a bond-alternant model, but not at all with those calculated for a planar, bond-equivalent model.

Theoretical Discussion

It is interesting that even after many years of study in the field, disagreement persists over the best definition of "aromaticity." A satisfactory theoretical description of the phenomenon has been developed,[35] and various experimental criteria for its presence have come to be accepted.[30,52] Difficulties seem to arise because quantities amenable to theoretical calculation cannot be easily experimentally determined, and *vice versa*. We have developed above a new, empirical, experimental criterion for aromaticity in hydrocarbons, the diamagnetic exaltation. This easily measured quantity can be related to an easily calculated theoretical quantity, the London diamagnetism,[53] and the following discussion develops that relationship.

The peculiar magnetic properties of aromatic compounds (besides exaltation there are large magnetic anisotropies and anomalous nmr chemical shifts) are widely held[30,35,52,54] to be results of the relatively large magnetic moments induced in the fully delocalized π-electrons characteristic of these systems. This has come to be called the "ring current."[55]

Contribution of ring current to susceptibility is a quantity amenable to theoretical calculation, and such calculations have been made[44,57] for a variety of aromatic compounds by the London method[53] or a modification of it. The values obtained thereby have usually been compared with the magnetic *anisotropy* data widely available for these compounds, but with rather poor agreement. In fact one can not expect agreement between the calculated "London" or ring-current diamagnetism and the magnetic anisotropy ΔK because the important contribution of Van Vleck paramagnetism to anisotropy is not included.[7,35,51] However, the London diamagnetism is related to exaltation, and should correlate with it. The relation is derived as follows.

The ring-current diamagnetism will make a contribution to the total susceptibility of a molecule; for planar aromatics, this contribution is made solely in a direction normal to the molecular plane.[35] For a molecule in a fluid medium, the molar susceptibility of a compound is given by[58]

$$\chi_M = \frac{1}{3}(K_x + K_y + K_z) \tag{2}$$

where K_x, etc., are orthogonal components of the susceptibility tensor, with z being taken normal to the molecular plane. Separating the London diamagnetism from the z component, we obtain

$$\chi_M = \frac{1}{3}(K_x + K_y + K_z' + K_L) \tag{3}$$

If we assume that aromatic compounds differ magnetically from polyenes only in the possession of a ring current we can rewrite (3)[59]

$$\chi_M = \chi_{M'} + \frac{1}{3}K_L \tag{4}$$

where $\chi_{M'}$ is the susceptibility of a cyclopolyene having the same formal structure as the aromatic. We have shown above that this can be estimated with good accuracy. From (1) and (4) we obtain[59]

$$\Lambda = \frac{1}{3}K_L \tag{5}$$

Recognize that (5) will be valid only to the extent that the assumption of essential magnetic equivalence between aromatic and nonaromatic compounds is correct; however, the two quantities should be at least proportional.

The London diamagnetism of benzene has been calculated by a number of theoretical methods, and the consensus of these results gives $K_L \approx 30$.[35,60] Dailey has shown[60] that a value of that magnitude gives ring-current chemical shifts for benzene and several benzenoid aromatics which agree with those observed. Applying (5) we obtain $K_L = 3\Lambda = 41$, a value which is near the theoretical maximum[35] (calculated by the Pauling method assuming a circle of radius 1.40 Å) and thus probably too large. This implies that (5) is probably only an approximate equation, and that the assumption discussed above is

---

(50) Generally these are referred to as values of "$\Delta K\pi$." This symbol is misleading; the anisotropy due to the π system contains a substantial contribution from the Van Vleck paramagnetism as well as the ring current.[35,51] The symbol K_L is preferable.

(51) J. D. Wilson, submitted for publication.

(52) F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garrat, K. Grohman, G. DiMaio, J. Mayer, M. V. Sargent, and R. Wolovsky, "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 75.

(53) F. London, *J. Chem. Phys.*, **5**, 837 (1937); *J. Chim. Phys. Radium*, **8**, 397 (1937).

(54) 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, Chapter 7.

(55) It is now clear that the ring current is not entirely responsible for the anisotropy or chemical shifts observed. "Local" effects and Van Vleck paramagnetism are also important.[35] Some even attribute the phenomena wholly to local effects.[56]

(56) J. I. Musher, *J. Chem. Phys.*, **41**, 2559 (1964); *Advan. Magnetic Resonance*, **2**, 177 (1967).

(57) R. McWeeny, *Proc. Phys. Soc.*, **A64**, 261 (1951); **64**, 921 (1951); **65**, 839 (1952).

(58) A. A. Bothner-By and J. A. Pople, *Ann. Rev. Phys. Chem.*, **16**, 43 (1965).

(59) J. Hoarau, *Ann. Chim., Ser. XIII*, **1**, 544 (1956).

(60) B. P. Dailey, *J. Chem. Phys.*, **41**, 2304 (1964).

Table III. Exaltations and London Diamagnetism Data for Aromatic Compounds

Compound	Λ/Λ(benzene)[a]	K_L/K_L(benzene)[b]
Benzene	1.00	1.000
Biphenyl	1.9	1.88
Terphenyl	2.9	2.74
Quaterphenyl	3.8	3.62
Biphenylene	1.0	−0.13, 0.72[c]
Naphthalene	2.2	2.22
Azulene	2.2	2.27
Anthracene	3.5	3.53
Phenanthrene	3.4	3.31
Tetracene	4.8	4.88
Chrysene	4.7	4.61
Pentacene	6.1	6.26
Dibenz[*a,h*]anthracene	5.1	5.58
Acenaphthylene	2.9	3.31
Pyrene	4.2	4.70
Fluoranthene	3.1	3.04
Triphenylene	3.6	4.33
Perylene	3.7	4.17
Coronene	7.5	10.13

[a] Calculated from the data of Table I. [b] B. Pullman and A. Pullman, "Les Theories Electronique de la Chimie Organique," Masson et Cie., Paris, 1952, p 545, except as otherwise noted. [c] Derived from the data of H. P. Figeys, *Chem. Commun.*, 495 (1967).

not completely accurate. However, the agreement is satisfactory.[61]

Values of the London diamagnetism relative to that of benzene are considerably easier to obtain theoretically than the absolute values of that quantity,[44] and data have been calculated for a variety of benzenoid aromatics. In Table III these are listed together with values of relative exaltations obtained in this work. These are seen to be quite comparable and thus we infer that $\Lambda \propto K_L$ even if (5) is not exact.

Finally note that in the discussion of the results (above) we mentioned several predictions made from theoretical calculations of K_L which were confirmed by or consistent with the exaltations found in this work. These provide additional evidence for the proportionality of Λ and K_L. Thus diamagnetic susceptibility exaltation is related directly to the London diamagnetism. It should prove to be a powerful tool to test the predictions of theory in this field.

Experimental Section

Materials. Cyclooctene, 1,3-cyclooctadiene, 1,5-cyclooctadiene, and cyclododecene (gifts from the Cities Service Research and Development Co.), cycloheptene (Aldrich Chemical Co.), cyclopentene (J. T. Baker Chemical Co.), cyclooctatetraene (gift of BASF, AG), and indene (Eastman) were distilled under reduced pressure before use.

1,3-Cycloheptadiene was prepared by the method of ter Borg and Bickel[62] and then fractionally distilled; its purity was established by glpc. 1,3,5-Cyclooctatriene was synthesized and purified by the method of Cope, *et al.*[63] 3,7,7-Trimethyl-1,3,5-cycloheptatriene was obtained by the method of Corey, *et al.*[64] 5,5-Dimethyl-1,3-cyclopentadiene was prepared by the method of Rouse and Tyler[65] and purified by glpc (Autoprep Model A-7000, DC-710 column). Cyclopentadiene was fractionally distilled from its dimer (Matheson Coleman and Bell) through a ten-theoretical-plate column and collected in a receiver cooled by Dry Ice. Cycloheptatriene was obtained commercially (Shell Chemical Co., practical grade). One sample of the crude 1,3,5-cycloheptatriene was fractionally distilled; a second sample was purified by glpc. Both of the samples contained less than 3% toluene as judged by their refractive indices. Heptalene was synthesized by the method of Dauben and Bertelli[18,66] and was freshly chromatographed over Woelm activity II neutral alumina (pentane eluent) in a nitrogen atmosphere before used. Heptafulvalene was prepared by the method of Doering and Mayer[67] and chromatographed over activity II neutral alumina using pentane as eluent. One sample used for susceptibility measurement contained 40% 7,7′-bis(cycloheptatrienyl), as determined by uv spectroscopy. 7,7′-Bis(cycloheptatrienyl) was prepared by Dr. F. R. Hunter[68] of these laboratories. Acepleiadiene was prepared following the procedure of Boekelheide, Langland, and Liu.[40] A sample of 1,4-cycloheptadiene supplied by Dr. W. Roth was distilled. A sample of biphenylene supplied by Professor L. Friedman was used as received. [16]Annulene, obtained from Dr. G. Schroder, was subjected to column chromatography (Woelm activity II neutral alumina, pentane eluent). All of the above compounds exhibited uv and nmr spectral properties consistent with their structures. All liquid samples were saturated with nitrogen and degassed on a vacuum line.

All solvents were purified by established methods[69] starting with commercial materials. The purity of solvents used as susceptibility standards was established by uv, nmr, and glpc. Dichloromethane, chloroform, acetonitrile, and benzene were saturated with nitrogen before use; the other solvents were degassed. Degassing a nitrogen-saturated organic liquid generally changed the volume magnetic susceptibility by no more than 0.5%.

Volume magnetic susceptibility determinations were made by two nmr methods.[70] The first method was essentially that of Frei and Bernstein[10] as modified by Mulay and Haverbusch.[11] The reference assembly[11] was contained within a precision-bore, 5-mm (o.d.) nmr tube obtained from the Wilmad Glass Co. The reference signals arising from the spherical and cylindrical portions of the reference assembly were examined independently on a Varian A-60 nmr spectrometer and their separation determined to ±0.1 Hz for each sample. The 50-Hz sweep-width chart setting was standardized at the time of each measurement with the chemical-shift difference of acetone and cyclohexane in carbon tetrachloride solution. This chemical-shift difference was determined to be 38.4 ± 0.1 Hz with a Varian DA-60-IL nmr spectrometer and a General Radio Model 1191 frequency counter. With the 50-Hz sweep-width setting, the A-60 consistently recorded this chemical-shift difference as 36.4 ± 0.1 Hz but, since all susceptibility measurements made by this technique were done with the same settings on the A-60, no corrective factor was applied. The probe temperature was determined at the time of each measurement. Using several standards of well-known susceptibility,[71] a linear plot of reference peak separation *vs.* volume diamagnetic susceptibility was readily obtained.[10,11] The calibration line of each reference

---

(61) It is probable that the set of increment values used to obtain $\chi_{M'}$ overestimates the contribution of Van Vleck paramagnetism to the susceptibilities of aromatics; benzene derivatives are generally more symmetrical than the various compounds used as models, and thus their paramagnetism should be smaller. Overestimation of this effect would cause Λ to appear larger than it "should be," and it is noteworthy here that benzene exhibits a somewhat larger exaltation than toluene or styrene, less symmetrical molecules.

(62) A. P. ter Borg and A. F. Bickel, *Rec. Trav. Chim.*, **80**, 1229 (1961).

(63) A. C. Cope and F. A. Hochstein, *J. Am. Chem. Soc.*, **72**, 2575 (1950); A. C. Cope, A. C. Haven, Jr., F. L. Ramp, and E. R. Trumbull, *ibid.*, **74**, 4867 (1952).

(64) E. J. Corey, H. J. Burke, and W. A. Remers, *ibid.*, **78**, 180 (1956).

(65) R. S. Rouse and W. E. Tyler, *J. Org. Chem.*, **26**, 3525 (1961).

(66) H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 4659 (1961); D. J. Bertelli Ph.D. Thesis, University of Washington, Seattle, Wash., 1961.

(67) W. von E. Doering, "Theoretical Organic Chemistry, The Kekule Symposium," Butterworths Scientific Publications, Ltd., London, 1959, p 42; J. R. Mayer, Ph.D. Thesis, Yale University, New Haven, Conn., 1957.

(68) F. R. Hunter, Ph.D. Thesis, University of Washington, Seattle, Wash., 1966.

(69) A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Topps, Jr., in "Technique of Organic Chemistry," Vol. VII, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1955, pp 297–459.

(70) For a detailed discussion of nmr methods for the determination of magnetic susceptibilities see J. L. Laity, Ph.D. Thesis, University of Washington, Seattle, Wash., 1968.

(71) S. Broersma, *J. Chem. Phys.*, **17**, 873 (1949); G. W. Smith, "A Compilation of Diagmagnetic Susceptibilities," General Motors Corporation Research Report GMR-317, Detroit, Mich., 1960; "Supplement to GMR-317," General Motors Corporation Research Report GMR-396, Detroit, Mich., 1963.

Table IV. Data for Calculating the Susceptibilities of Neat Liquids

Compound	κ	Method	ρ	χ
Cyclopentene	0.562	2	0.771	0.729
Cyclopentanol	0.709	2	0.948	0.748
1,3-Cyclopentadiene	0.540	2	0.786	0.687
5,5-Dimethyl-1,3-cyclopentadiene	0.549	1	0.7656	0.717
	0.552	2	0.768	0.718
Cycloheptene	0.593	2	0.822	0.720
1,3-Cycloheptadiene	0.558	2	0.861	0.648
1,4-Cycloheptadiene	0.552	1	0.851	0.648
1,3,5-Cycloheptatriene	0.617	2	0.943	0.655
	0.596	2	0.932	0.640
3,7,7-Trimethyl-1,3,5-cycloheptatriene	0.5995	1	0.8405	0.713
Cyclooctene	0.618	2	0.844	0.731
1,3-Cyclooctadiene	0.584	2	0.868	0.673
1,5-Cyclooctadiene	0.588	2	0.888	0.661
1,3,5-Cyclooctatriene	0.550	2	0.897	0.613
Indene	0.6715	1	0.9837	0.683
Cyclododecene	0.674	2	0.878	0.767

Table V. Data for Calculating Susceptibilities of Solutions

Compound	κ	Method	f_a	Solvent	χ_s	ρ	χ_a
Biphenylene	0.620	1	0.1780	Benzene	0.708	0.9085	0.562
	0.684	1	0.0725	CCl_4	0.433	1.539	0.58
	0.622	1	0.1838	Benzene	0.708	0.9077	0.582
[16] Annulene	0.589	1	0.1895	Benzene	0.702	0.8856	0.507
	0.594	1	0.1104	Benzene	0.702	0.8744	0.50
3,5-Dimethylaceheptalene	0.6025	1	0.1286	Benzene	0.708	0.8764	0.548
	0.6015	1	0.1311	Benzene	0.702	0.8847	0.548
	0.602	1	0.1337	Benzene	0.708	0.877	0.543
2-Phenyl-5,7-dimethylpleiapentalene	0.631	1	0.1774	Benzene	0.708	0.9022	0.664
	0.524	1	0.0240	CH_3CN	0.682	0.768	0.67
	0.623	1	0.1328	Benzene	0.708	0.8827	0.700
	0.628	1	0.1907	Benzene	0.708	0.8900	0.695
Heptalene	0.675	2	0.016	CCl_4	0.433	1.564	0.35
	0.681	2	0.070	CCl_4	0.433	1.560	0.484
trans-15,16-Dimethyl-15,16-dihydropyrene	0.646	1	0.0973	Benzene	0.702	0.895	0.92
	0.708	1	0.0384	CCl_4	0.433	1.565	0.91
1,3,6,8,15,16-Hexamethyl-15,16-dihydropyrene	0.621	1	0.0848	Benzene	0.702	0.864	0.89
	0.608	1	0.0306	Benzene	0.702	0.8626	0.85
Acepleiadiene	0.870	2	0.110	CH_2Br_2	0.360	2.204	0.676
	0.858	2	0.107	CH_2Br_2	0.360	2.200	0.640
Acepleiadylene	0.738	2	0.068	CH_2Cl_2	0.549	1.308	0.77
	0.744	2	0.082	CH_2Cl_2	0.549	1.310	0.78
7,7′-Bis(cycloheptatrienyl)	0.843	2	0.127	CH_2Br_2	0.369	2.071	0.669
Heptafulvalene–7,7′-bis(cycloheptatrienyl) (60:40)	0.672	2	0.060	CCl_4	0.428	1.540	0.567

tube was determined using a modified version of a linear least-squares computer program given by Wiberg[72] and an IBM 7090-7094 computer system. Thus, for measurements obtained at 36.0–36.5° on the A-60 for a reference assembly containing tetramethylsilane, seven standards (nitromethane, acetonitrile, ethanol, benzene, water, bromoform, and methylene iodide) gave a calibration equation for volume magnetic susceptibility κ (in units of -10^{-6}) and reference peak separation, n (Hz), of $\kappa = 0.00962n + 0.5306$ with a standard deviation in κ of 0.0014. Such a calibration equation allows the calculation of the volume magnetic susceptibility of any sample from the separation n observed when it is in the sample tube. Since the uncertainty in each measurement of n is 0.1 Hz, the standard error in each determination of κ is approximately 0.001. The accuracy and precision of this method is thus found to be equal to that obtained by classical magnetic balance methods.[73]

The second nmr method used for the determination of volume magnetic susceptibilities was that perfected by Douglass and Fratiello.[12] The susceptibility cells were obtained from Wilmad Glass Co. Toluene was used as the reference liquid, and measurements were obtained with a Varian DP-60 nmr spectrometer operating in the HR mode at a probe temperature of 25.0°. Peak separations were determined (generally with an uncertainty of 1 Hz) by sidebanding techniques using a Hewlett Packard Model 521C electronic counter. The DP-60 was operated by Mr. B. J. Nist. For 11 samples of well-known susceptibility (methanol, *n*-hexane, ethanol, benzene, toluene, carbon tetrachloride, water, dichloromethane, 1,2-dichloroethane, and dibromomethane), the suscepti-

---

[72] K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964, p 535.

[73] *Cf.* ref 13, pp 3–29 and L. N. Mulay, *Anal. Chem.*, **34**, 343R (1962).

bility cell gave a calibration equation (obtained as above) of $\kappa = 0.00237n + 0.4672$ with a standard deviation in κ of 0.004. This method clearly bears a larger experimental uncertainty than the first nmr method, but is particularly useful for measurements on samples containing highly volatile or reactive components (since the tubes are readily sealed) or for determinations made on powdered solids.

The density of each sample was determined in a water bath at the same temperature (within 0.1°) as the probe temperature at the time of the volume magnetic susceptibility measurement. Lipkin bicapillary pycnometers of 0.25, 0.5, and 1 ml sizes (Ace Glass Co.) were calibrated with triply distilled water and used in accordance with the procedures exhaustively discussed by other workers.[74] Density values were thus generally obtained with a precision of 0.0005 g/cc.

Solutions. Solutions for magnetic susceptibility determinations were prepared by weighing appropriate quantities of solute and solvent to the nearest 0.1 mg in 5-ml stoppered vessels. Concentrations were expressed as weight fractions. Once prepared, solutions were treated in the same manner as other liquid samples; all possible care was taken to maintain constant concentrations. The Wiedemann additivity law[13,75] was applied to determine the susceptibility of a solute from that of the solution. For the compounds of this study, the only solvent found to give deviations from Wiedemann's law was dimethyl sulfoxide.[18]

Formulas and Data. The magnetic susceptibility per gram, χ, of a pure compound is expressed by $\chi = \kappa/\rho$ where κ and ρ represent, respectively, the volume magnetic susceptibility (units of -10^{-6}) and the density (units of cm^3/g). For a solution measurement, χ_a, the per gram susceptibility of the solute, is given[18] by the equation $\chi = (\kappa/\rho) - \chi_s(1 - f_a)/f_a$ where κ and ρ are as defined above and obtained for the solution, f_a is the weight fraction of the solute, and χ_s is the per gram susceptibility of the solvent. The molar susceptibility, χ_M, is defined as $\chi_M = M\chi$ where M is the molecular weight of the substance in grams; the units of χ_M are -10^{-6} cm^3/mol. Table IV presents the data used in calculating the molar susceptibilities of several neat liquids, and Table V contains the data for solutions. In Table V two values are given for the mass susceptibility of benzene; 0.708 is the susceptibility of benzene saturated with nitrogen, and 0.702 is the value for benzene saturated with air.[13]

Acknowledgment. We wish to thank Dr. D. C. Douglass, Dr. R. F. Zürcher, Professor H. A. Staab, and Professor V. Schomaker for advice on experimental techniques, and Professor A. G. Anderson, Professor V. Boekelheide, Professor L. Friedman, Professor K. Hafner, Dr. W. Roth, Dr. G. Schröder, and Professor E. Vogel for supplying samples used in this study. We also thank Professor Anderson and Dr. J. L. Sprung for critical evaluation of portions of this paper. J. D. W. thanks the National Science Foundation for the grant of a Fellowship. This work was supported in part by the U. S. Army Research Office (Durham) and the National Science Foundation.

---

(74) M. R. Lipkin, J. A. Davison, W. T. Harvey, and S. S. Kurtz, Jr., *Ind. Eng. Chem., Anal. Ed.*, **16**, 55 (1944); N. Bauer and S. Lewin in "Technique of Organic Chemistry," Vol. I, Part I, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1955, p 131.

(75) L. N. Mulay in "Treatise on Analytical Chemistry," Vol. IV, Part I, I. M. Kolthoff and P. J. Elving, Ed., John Wiley & Sons, Inc., New York, N. Y., 1963, p 1783.

The Absolute Configuration of Pinacolyl Alcohol[1]

John Jacobus, Zdenko Majerski, Kurt Mislow, and Paul von Ragué Schleyer

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received November 15, 1968*

Abstract: The absolute configuration of (+)-pinacolyl alcohol (**1**), although widely assumed to be (*S*), has never been firmly established and there is reason to question the usual assignment. Direct chemical correlation with (+)-(*S*)-lactic acid firmly establishes that the absolute configuration usually assumed is indeed correct. The key step in the chemical correlation (Chart I) was the construction of the *t*-butyl group by hydrogenolysis of a 1-methyl-1-cyclopropane derivative (**4**).

Optically active pinacolyl alcohol (3,3-dimethyl-2-butanol, **1**) has been frequently employed in asymmetric syntheses,[2] yet its absolute configuration, though widely assumed to be (+)-(*S*) on the basis of indirect physical[3] and chemical[4] evidence, has never been rigorously established. However, the physical evidence has been termed "not entirely convincing."[5] There is at least one case on record,[6] as far as chemical evidence[4] is concerned, in which an apparent inconsistency involving **1** has been encountered: whereas methyl ketones (CH_3COR, R = C_2H_5, *i*-C_3H_7, C_6H_5) yield alcohols of

---

(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B, by the National Institutes of Health (AI-07766), the National Science Foundation, and the Petroleum Research Fund, administered by the American Chemical Society.

(2) (a) H. S. Mosher and E. La Combe, *J. Am. Chem. Soc.*, **72**, 3994 (1950); (b) L. M. Jackman, J. A. Mills, and J. S. Shannon, *ibid.*, **72**, 4814 (1950); (c) H. S. Mosher and E. La Combe, *ibid.*, **72**, 4991 (1950); (d) V. Prelog, E. Philbin, E. Watanabe, and M. Wilhelm, *Helv. Chim. Acta*, **39**, 1086 (1956); (e) H. S. Mosher and P. K. Loeffler, *J. Am. Chem. Soc.*, **78**, 4959 (1956); (f) V. Prelog and H. Scherrer, *Helv. Chim. Acta*, **42**, 2227 (1957); (g) P. Newman, P. Rutkin, and K. Mislow, *J. Am. Chem. Soc.*, **80**, 465 (1958); (h) W. M. Foley, F. J. Welch, E. M. La Combe, and H. S. Mosher, *ibid.*, **81**, 2779 (1959); (i) K. Mislow, R. E. O'Brien, and H. Schaefer, *ibid.*, **82**, 5512 (1960); (j) O. Červinka, *Collection Czech. Chem. Commun.*, **30**, 1684 (1965); (k) M. M. Green, M. Axelrod, and K. Mislow, *J. Am. Chem. Soc.*, **88**, 861 (1966); (l) J. Sauer and J. Kredel, *Tetrahedron Letters*, 6359 (1966); (m) O. Červinka, O. Bělovský, A. Fábryová, V. Dudek, and K. Grohman, *Collection Czech. Chem. Commun.*, **32**, 2618 (1967).

(3) Through application of the Freudenberg Displacement Rule (P. G. Stevens, *J. Am. Chem. Soc.*, **55**, 4237 (1933)).

(4) The chemical evidence has consisted of configurational correlations which, implicitly or explicitly, have involved comparisons of topographies of diastereomeric transition states in asymmetric syntheses.[2]

(5) J. A. Mills and W. Klyne, *Progr. Stereochem.*, **1**, 206 (1954).

(6) H. C. Brown and D. B. Bigley, *J. Am. Chem. Soc.*, **83**, 3166 (1961).