

EVIDENCE FOR PARAMAGNETIC EXALTATION IN A $4n-1$ -ELECTRON, $(4n-2)$ -ATOM,
CONJUGATED MACROCYCLE.

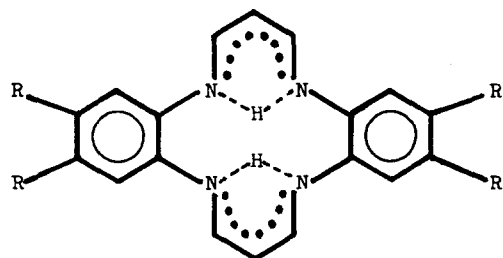
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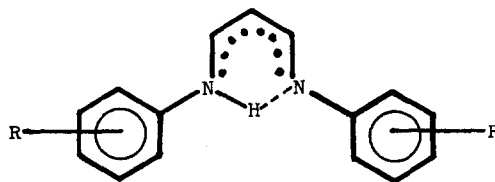
(Received in UK 2 July 1974; accepted for publication 18 July 1974)

An accurate study of the magnetic susceptibilities of paramagnetic complexes of the macrocycle I dictates the need for reliable information concerning its molar diamagnetic susceptibility χ_M . If tabulated constants are to be used¹ to give an estimated susceptibility (χ'_M), then appeal must be made to spectroscopic properties in order to establish the most appropriate structural formula. For large molecules it is more satisfactory to measure χ_M directly. The values for χ_M and χ'_M of I differ by substantially more than experimental error.

The proton magnetic resonance (PMR) and electronic spectra of I and related malondianils^{3,4} and benzodiazepinium salts⁴ indicate the equivalence of the 1,3-carbon atoms in the di-imine bridge and the full conjugation of the latter. A detailed PMR study at 60 MHz was facilitated by the high solubility, in chloroform, of the new tetramethyl derivative of I (namely, compound II), synthesised by published methods². The results of this study are presented in the Table, and clearly establish the equivalence of the 1,3-carbon atoms^{2,3,4}. The fact that the NH protons appear as a triplet ($J=6$ Hz) at 60 MHz implies either that they occupy a bridging position between two nitrogen atoms thereby undergoing a trans - coupling to two equivalent CH protons, or that there is slow exchange of these protons between two CH \cdots N sites having chemical shifts differing by 6 Hz, thus producing a chance superposition of two $J=6$ Hz doublets. The retention of the triplet structure with $J=6$ Hz in solvents with high dielectric constant at 60 MHz and in deuteriochloroform at 100 MHz lends support to the former suggestion. The strength of such intramolecular NH \cdots N interactions has recently been remarked upon⁵. The triplet structure of the 1,3-CH signal arises from the chance coincidence between J_{cis} CH \cdots CH and J_{trans} CH \cdots N...H; this is confirmed by the collapse of this signal to a 1:1 doublet with $J=6$ Hz upon irradiation at a frequency appropriate to either the NH or 2-CH signals. The elongation of the NH bond, implied by the



I: R = H

II: R = CH₃

III

bridging model, is expected to reduce the value of $J_{\text{trans}} \text{CH} \cdots \text{N} \cdots \text{H}$ below the characteristic value of circa 12Hz observed for malondianil hydrochloride in an all-trans configuration³. The bridging model does however, maintain a substantial s-atomic orbital electron charge density at the NH proton, which could account for the observed reduction of only 50% in J_{trans} . The structural formula selected for I, and used as a basis for application of Haberditzl's¹ or Pascal's constants⁶, is therefore that depicted in the Figure.

If the experimental value¹ for two moles of benzene ($-2 \times 54.8 \times 10^{-6}$ cgs emu⁷) is taken as a starting point, the replacement of four protons by two 1,3-di-imine bridges gives either $\chi'_{\text{M}}(\text{H}) = -157 \times 10^{-6}$ cgs emu or $\chi'_{\text{M}}(\text{P}) = -163 \times 10^{-6}$ cgs emu by using the constants of Haberditzl or Pascal respectively. The hydrogen bridged, six-membered, six π -electron "ring" is treated as a pyrimidine ring so that tabulated values of Pascal's constitutive corrections can be used. If Pascal's constants are used throughout, instead of using the χ_{M} of benzene as a starting point, the identical value for $\chi'_{\text{M}}(\text{P})$ is obtained. To permit the use of Haberditzl's constants, the di-imine "ring" is considered to have two N-H bonds, no non-bonding lone pairs, and C \cdots C⁸ and C \cdots N bonds at 2/3 ethylenic π -character. The use of the χ_{M} of benzene circumvents the problem of estimating the Haberditzl diamagnetic exaltation for a complicated benzene derivative¹. These estimates of χ'_{M} contrast with the experimental value (χ_{M}) of -140×10^{-6} cgs emu. Even the estimates for the localised azomethine, en-amine form of I (bridging H atoms retained) are substantially more negative than the experimental value. For example, Pascal's constants give a value ranging from -148×10^{-6} to -153×10^{-6} cgs emu depending upon the choice of C=N parameter, and Haberditzl's constants give an identical range of values depending upon the assumed number of non-bonding lone pairs. The above data is compatible with the presence of a

paramagnetic contribution to χ_M , associated with the conjugated $4n\pi$ -electron, $(4n-2)$ atom inner great ring of I.

A comparison between the chemical shifts of protons in II and those of analogous protons in three related dimethyl malondianils (III) is presented in the Table. The downfield shift of the inner protons and the slight upfield shift of the outer protons in II is reminiscent of the behaviour of [16]-annulene⁹. Detailed calculations¹⁰ on I and malondianil show that it is most unlikely that the observed inner and outer proton shifts are caused by differences in either π -electron or valence electron charge densities. Further, evidence for 20% ring delocalisation in a related macrocycle has been presented recently¹¹ and the relationship between the PMR of diphenyl formazan¹² and an octa-aza dihydro[16]-annulene¹³ is similar to that between malondianils and I or II.

Longuet-Higgins¹⁴ has described how lifting the degeneracy of the highest occupied orbitals in [16]-annulene can lead to paramagnetic exaltation. In polygonal [16]-annulene the two lowest empty molecular orbitals are degenerate. We suggest that paramagnetic exaltation in 14-atom, 16π -electron inner great ring macrocycles arises through the lifting of this degeneracy and the introduction of two extra π -electrons imposed by the substitution of two =N- and two -NH- units for four =CH- units in [16]-annulene.

Protons	II	III R = o-Me	III R = m-Me	III R = p-Me	Type of proton	Approximate shift δ
2-(CH)	5.10 (triplet, 6Hz)	4.85 (broad)	4.95 (broad)	4.98 (triplet, 7Hz)	Outer	0.1 upfield
1,3-(CH)	2.42 (triplet, 6Hz)	2.40 (broad)	2.35 (doublet, 7Hz)	2.35 (doublet, 7Hz)	Outer	0.05 upfield
CH ₃	7.87	7.66	7.70	7.70	Outer	0.15 upfield
Aromatic	3.22	3.0	3.08	2.95	Outer	0.15 upfield
NH	-3.80 (triplet, 6Hz)	-2.5	-2.4	-2.4	Inner	1.3 DOWNFIELD

δ (Shift observed upon transfer from linear to macrocyclic species.)

Table. PMR chemical shifts for some conjugated species in CDCl₃ solution (60MHz; τ -units)

The molar magnetic susceptibilities of such ring systems^{2,5,11,13} should either be measured, or be estimated with the incorporation of a ring-correction term of the order of $+ 2 \times 10^{-5}$ cgs emu. This latter allows for a contribution opposite in sign¹⁵ to the so-called diamagnetic ring current characteristic of Hückel aromatic systems with $4n + 2$ π -electrons¹. It would be of great value to obtain and study macrocycles with a 14-atom 14- π -electron tetraaza inner great ring, such as TATA discussed in Ref.10, to discover whether the anticipated (and attenuated¹⁵) diamagnetic exaltation is indeed present. Only then could the possibility of lone pair paramagnetic effects be eliminated as the cause of the paramagnetic exaltation in I; the data presented above does not favour such an interpretation.

Acknowledgements Drs. A. Earnshaw and P. Burchill are thanked, respectively for magnetic measurements and sample preparation.

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