$Rh_6(CO)_{16}$ is an exception to the "inert gas rule" for the polynuclear metal carbonyls in that the entire molecule contains two electrons in excess of the "xenon" configuration for each rhodium atom. The observed spin-pairing of all electrons[15] can be *rationalized* from a consideration of LCAO MO symmetry arguments based on an assumed localized D_{4d} antiprismatic configuration. Sixteen of the $18^1/_3$ electrons per rhodium are utilized in filling the eight σ-bonding arbitals.[17] The problem then resolves into placing the remaining $2^1/_3$ electrons per rhodium (or seven electron-pairs for the six rhodiums) into appropriate antibonding MO's which are assumed to possess mainly the characteristics of the metal AO's. From the presumed energetics of the tetragonal antiprismatic system,[18] the rhodium-like orbitals available for bonding with one another are the lowest-lying d_{z^2} and the next lowest degenerate $(d_{x^2-y^2}, d_{xy})$ MO's. From the d_{z^2} orbitals for the six rhodiums one can form six linear combinations which under octahedral (O_h) symmetry split to give a_{1g}, e_g and t_{1u} levels. Since the d_{z^2} orbital for each rhodium apparently lies considerably below the other orbitals due to its antiprismatic environment, it is reasonable that all of these levels are occupied with six electron-pairs. Likewise, the six $d_{x^2-y^2}$ orbitals give rise to a_{2g}, e_g and t_{2u} and the six d_{xy} orbitals yield a_{2u}, e_u and t_{2g}. From overlap considerations it appears that the lowest of these six energy levels is the a_{2u}, and hence the remaining electron-pair will occupy a non-degenerate level. Since this electron-pair is strongly delocalized and has low-lying excited levels, both the spin-pairing and the intense absorption of this black compound can be explained. Of obvious significance is whether these two electrons can be selectively removed to give $Rh_6(CO)_{16}{}^{1+}$ and $Rh_6(CO)_{16}{}^{2+}$ species.

It should be noted that the unpaired electron in $(C_5H_5)_3Ni_3(CO)_2$ which also formally must lie in an antibonding MO with respect to the $C_5H_5{}^{1-}$ and CO ligands has been assigned on the basis of electron spin measurements[19] to a π-bonding combination of essentially 3d orbitals on the nickel atoms. For $Rh_6(CO)_{16}$, however, the antibonding π-type (d_{xz}, d_{yz}) MO's for a tetragonal antiprismatic arrangement appear to be energetically unfavorable and furthermore, a combination of such orbitals under octahedral symmetry would lead to a lowest-lying degenerate "spin-free" state. It then would be necessary to invoke the Jahn–Teller theorem to obtain a "spin-paired" electronic configuration in the ground state. Within experimental error no molecular distortion is observed.

The molecular structure is in complete accord with the observed infrared spectrum[20] which shows two bands in the terminal carbonyl region at 2073 and 2026 cm.$^{-1}$ and one band at 1800 cm.$^{-1}$ which may be assigned to the bridged carbonyls each bonded to three rhodium atoms. A vibrational analysis reveals that the T_d structure predicts two infrared-active terminal C–O

stretching frequencies (both of F_2 symmetry) and one infrared-active asymmetric bridge C–O stretching frequency (F_2 symmetry). As assignment also can be made with the assumption that the coupling between the terminal carbonyl groups attached to different rhodium atoms can be neglected. Each $Rh(CO)_2$ fragment of localized C_{2v} symmetry would then give rise to two infrared-active terminal C–O stretching fundamentals of A_1 and B_1 representation; the symmetric mode (A_1) should correspond to the higher frequency (*i.e.*, 2073 cm.$^{-1}$) and the antisymmetric mode (B_1) to the lower frequency (*i.e.*, 2026 cm.$^{-1}$).[21,22]

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RECEIVED JANUARY 26, 1963

BURNAMICINE, A CRYPTOPINE-LIKE ANALOG OF CORYNANTHEOL

Sir:

The alkaloids of *Hunteria eburnea* Pichon have been the subject of a detailed examination[1,2] and have yielded 23 bases, among which were discerned representatives of new classes of indole alkaloids, in particular the eburnamine group[3] and the quaternary diastereoisomeric N_b-methyl derivatives of hunterburnine.[4] Although several examples of yohimbinoid bases were found in the quaternary base fraction,[1,4] none were recognized until now among the tertiary bases,[2] and the results to be described below allow us to put forward the structure I for burnamicine,[2] making it not
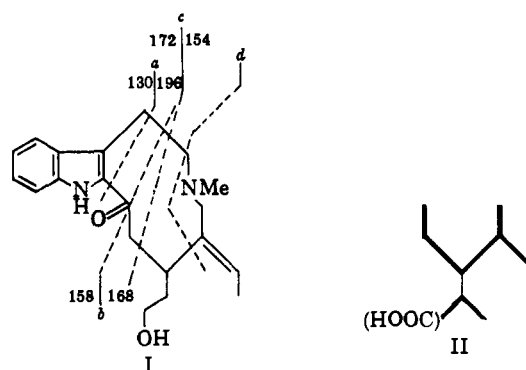
only the equivalent in indole alkaloids of cryptopine in isoquinoline alkaloids, but also the first representative of yet another variant of the formal yohimbinoid precursor II.[5] This knowledge may be of importance

(15) Magnetic susceptibility measurements[16] on $Rh_6(CO)_{16}$ show that it is very slightly paramagnetic. The susceptibility is not field dependent and shows no change on cooling from room temperature to 90°K. Since a value of 0.29×10^{-6} e.m.u./g. is obtained, it is concluded that there are no free spins and that the observed paramagnetism comes from small orbital contributions.

(16) We wish to thank Drs. F. J. Darnell and D. Flippen of the Central Research Department, E. I. du Pont de Nemours and Co., for carrying out this study for us.

(17) Each rhodium possesses a ninth orthogonal valence σ-type orbital made up primarily of the d_{z^2} AO which is directed along a 4-axis of $Rh_6(CO)_{16}$ toward the center of the molecule. The degenerate (d_{xz}, d_{yz}) AO's are π-type orbitals while the degenerate $(d_{x^2-y^2}, d_{xy})$ AO's are δ-type orbitals (referred to the principal symmetry axis).

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(2) M. F. Bartlett, R. Sklar, A. F. Smith and W. I. Taylor, in preparation.

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(4) J. D. M. Asher, J. M. Robertson, G. A. Sim, M. F. Bartlett, R. Sklar and W. I. Taylor, *Proc. Chem. Soc.*, 72 (1962); C. C. Scott, G. A. Sim and J. M. Robertson, *ibid.*, 355 (1962).

(5) E. Schlittler and W. I. Taylor, *Experientia*, 18, 244 (1960).
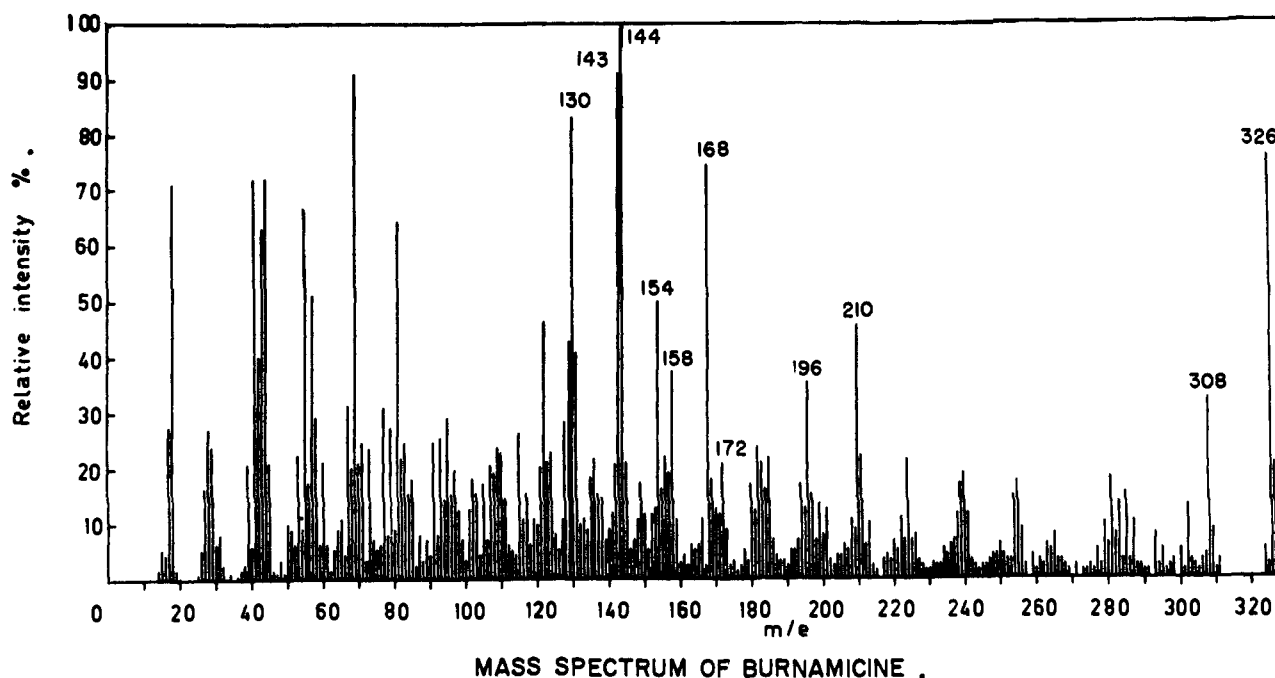
MASS SPECTRUM OF BURNAMICINE .

Figure 1.

for a better understanding of the growing number of alkaloids which contain 2-acylindole chromophores.[6]

Burnamicine had m.p. 198–200°, $[\alpha]_D$ −281°, $\nu_{C=O}^{KBr}$ 1630 cm.$^{-1}$,[7] pK_a 8.9 (50% aqueous methanol) [Found: mol. wt. (mass spectr.[8]), 326; C, 73.23, 73.07; H, 8.04, 8.09; N, 8.74; OMe, 0.0; NMe, 4.81; active H, 0.61. Calcd. for $C_{20}H_{26}N_2O_2$: mol. wt., 326; C, 73.59; H, 8.03; N, 8.58; NMe, 4.64; active H, 0.64%]. Its ultraviolet absorption spectrum [λ_{max} 309–312 mμ (ϵ = 14,600)] changed to that of a typical indole by either sodium borohydride reduction or solution in acid, and in the latter experiment the original chromophore was regenerated upon basification. In the p.m.r. spectrum[9] the four aromatic protons, the ethylidene group and the N-methyl were identifiable. The alkaloid recovered from the p.m.r. measurement was acetylated, and its ultraviolet and infrared spectra were consistent with an N_a, O-diacetate, and the p.m.r. spectrum showed besides the singlet methyls that there was a triplet centered at 4.14 p.p.m., in agreement with —CH$_2$—CH$_2$·OAc.

The interpretation of the mass spectrum (Fig. 1) of burnamicine was completely consistent with structure I. The predicted fissions[10] were observed and gave (with hydrogen transfer right to left) for a, m/e 130 (very strong) and 196; for b, 158 and 168 (very strong); and c, 172 and 154. Strong peaks at m/e 168, 130 and 144 (strongest peak in the spectrum) probably arose from the very facile extrusion of carbon monoxide (m = 28) from fragments m/e 196, 158 and 172. The

second strongest peak in the spectrum, m/e 143, could have arisen from a c-fission to yield m/e 171 then loss of carbon monoxide, or alternatively by fission of a parent ion–carbon monoxide (M-28) ring contracted ion. Other observed peaks result from the loss of the elements of water[10] from various fragments. Thus, loss of water from the parent ion gave a medium strength peak at m/e 308 which by a d-type fragmentation and loss of a hydrogen yielded m/e 210. The double bond was important in all of these processes because the end products were stable allylic radicals or ions[10] and peaks resulting from the loss of hydroxyethyl and/or CH$_2$·-NCH$_3$ could also be picked out.

No burnamicine remained either for further study of the mass spectra of derivatives or for a trivial conversion into dihydrocorynantheol methochloride,[11] and preliminary experiments to realize the converse have not yet been successful.

(11) If the proposed structure of vobasine is correct (ref. 6), then lithium aluminum hydride reduction of either it or isovobasine followed by acid treatment should yield macusine B.

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(6) Only in one other case, viz., vobasine and its dihydro derivatives, dregamine and tabernaemontanine, have any detailed formulas been proposed: U. Renner and D. A. Prins, Chimia, 15, 321 (1961).

(7) Correct for a 2-acylindole, J. A. Ballantine, C. B. Barrett, R. J. S. Beer, B. G. Boggiano, S. Eardley, B. E. Jennings and A. Robertson, J. Chem. Soc., 2229 (1957); M. F. Bartlett, D. F. Dickel and W. I. Taylor, J. Am. Chem. Soc., 80, 126 (1958).

(8) Kindly run for us by Dr. R. Ryhage.

(9) The spectra were run in deuteriochloroform by Dr. A. Z. Zücher using a Varian HR60 with tetramethylsilane as internal standard.

(10) These are processes where the resulting ion or radical is stabilized by an adjacent π bond (aromatic system, double bond, carbonyl) or electron pair on N_b. Extrusion of carbon monoxide was also an important process. The observed loss of water was probably the result of ring closure and not of double bond formation. For detailed discussion of the application of mass spectrometry to alkaloid chemistry, see K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapters 3 and 8.

RING INVERSION IN CYCLOÖCTANE

Sir:

The single line in the n.m.r. spectrum of cyclooctane has been reported[1,2] to broaden at temperatures below −85°. Harris and Sheppard estimated the coalescence temperature to be −153°, and the activation energy of ring inversion to be 2.6 kcal./mole. Meiboom suggested the existence of two different line-broadening processes, both with similar activation energies of about 8 kcal./mole.

Strong coupling among many protons of similar chemical shift complicates the low temperature spectrum of cyclooctane (Fig. 1). A simple proton magnetic resonance spectrum was obtained by preparation

(1) R. K. Harris and N. Sheppard, Proc. Chem. Soc., 418 (1961).

(2) S. Meiboom, paper presented at the Symposium on High Resolution Nuclear Magnetic Resonance at Boulder, Colorado, July, 1962.