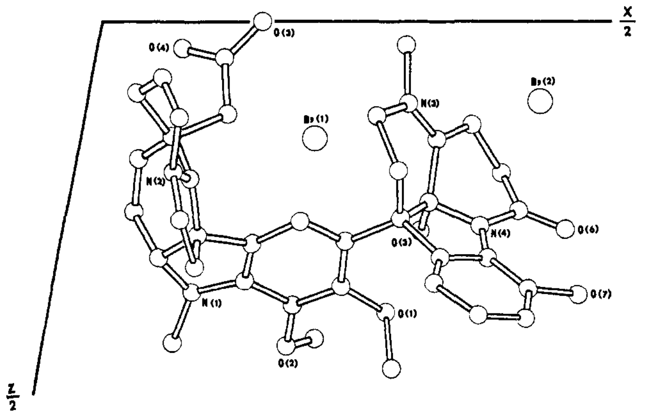
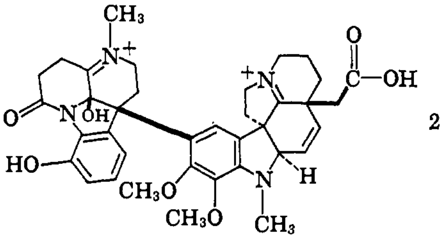


Figure 1.

A single-crystal X-ray diffraction study of haplophytine dihydrobromide revealed the structure shown in III (see Figure 1). The following crystal data were obtained for the dihydrobromide with Cu Kα radiation: monoclinic, space group C2, with a = 25.535, b = 7.490, c = 18.861 A, β = 101° 19′, V = 3537.2 A^3, Z = 4, D_x = 1.530, D_m = 1.528 g/cm^3.

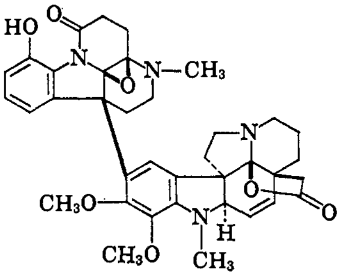


III

Three-dimensional diffraction intensity data were recorded at room temperature on a Picker four-circle automatic diffractometer for 2001 independent reflections. The positions of the bromine atoms in the unit cell were deduced from a three-dimensional Patterson synthesis. After fixing the origin of the unit cell by setting the y coordinate of one of the bromine atoms at zero, the positions of these heavy atoms were used to calculate the phases of the observed structure amplitudes. Successive three-dimensional Fourier syntheses and structure factor calculations progressively disclosed the electron-density distribution of the molecule. The R factor $(\Sigma||F_o| - |F_c||)/|F_o|$, is 8.4% with anisotropic temperature factors for the bromine atoms and isotropic for the light atoms excluding hydrogen. The bond distances and angles are within the range of accepted values.

There are two intramolecular hydrogen bonds in the molecule, as indicated by oxygen–oxygen distances of 2.6 A. One of these is in the 7-hydroxy-1-acylindole system, and the other is between the tertiary alcoholic hydroxyl group and the oxygen atom of the most proximal methoxyl group. The effect of the latter bond is to fix the orientation of the two large moieties with respect to one another in the crystal lattice. The absolute configuration of the molecule was determined by the anomalous dispersion method and is as shown in III and in the accompanying perspective diagram, in which the positive y direction extends out of the page toward the viewer (*i.e.*, conventional right-handed coordinate system). Further refinements of the structure will be reported in detail in due course.

Consideration of structure III in relation to the chemical and spectroscopic properties of haplophytine and the observation that the dihydrobromide is reconverted to the latter at pH 8 lead to the assignment of structure IV to haplophytine. This structure also permits the assignment of structures to the transformation products of haplophytine described earlier.[2]



IV

Acknowledgment. Acknowledgment is gratefully made by P. Y. to the National Research Council of Canada for a grant which supported this work in part.

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Trimethylenemethane, $C(CH_2)_3$

Sir:

Theoretical treatments[1,2] of trimethylenemethane (II) predict a triplet ground state and a high delocalization energy relative to the classical structure of one double bond and two localized electrons. Trimethylenemethane, stable in low-temperature matrixes, has recently been prepared by the photolysis of 4-methylene-1-pyrazoline[3a] or 3-methylenecyclobutanone,[3b] and the esr spectrum confirmed a triplet ground state. Trimethylenemethane and its derivatives have been postulated to explain the formation of "rearranged" methylenecyclopropanes in the pyrolyses[4] or photolyses[5] of 4-alkylidene-1-pyrazolines and in the thermal isomerization of methylenecyclopropanes.[6]

We have examined the gas-phase reaction of 2-iodomethyl-3-iodopropene (I)[7] with alkali metal vapor

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[1] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 43.

[2] D. P. Chong and J. W. Linnett, *J. Chem. Soc.*, 1798 (1965).

[3] (a) P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966); (b) P. Dowd and K. Sachdev, *ibid.*, **89**, 715 (1967).

[4] R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966).

[5] (a) A. C. Day and M. C. Whiting, *J. Chem. Soc., Sect. C*, 464 (1966); (b) S. D. Andrews and A. C. Day, *Chem. Commun.*, 667 (1966).

[6] (a) J. K. Crandall and D. R. Paulson, *J. Am. Chem. Soc.*, **88**, 4302 (1966); (b) J. P. Chesick, *ibid.*, **85**, 2720 (1963); (c) E. F. Ullman, *ibid.*, **82**, 505 (1960).

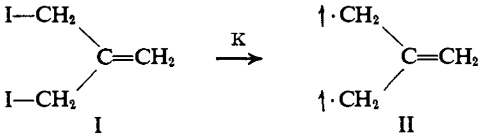
[7] 2-Iodomethyl-3-iodopropene (mp 32–33°, bp 83–85° (10 mm)) was prepared by the reaction of KI in acetone on 2-chloromethyl-3-chloropropene (see ref 8).

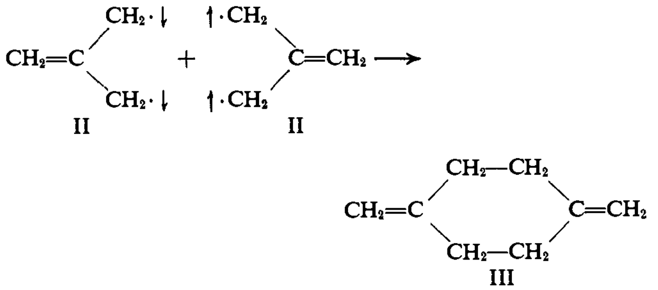
as a possible method of generating trimethylenemethane (II). The diiodide I was vaporized and carried in a helium stream, which was then saturated with alkali metal vapor by passage through a fine spray of sodium–potassium alloy (<10 sec in the spray zone) at 228–267°. The products consisted of 1,4-dimethylenecyclohexane (III),[9] *p*-xylene, isobutene (IV), 1-butene, *cis*- and *trans*-2-butenes, and methylenecyclopropane.[8]

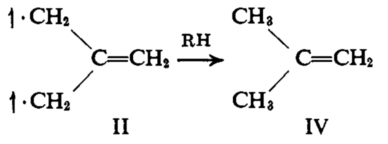
The sum of the yields of III and *p*-xylene remained constant from one reaction to another, totaling about 35%. However, their ratio varied considerably, suggesting that III is converted to *p*-xylene.

The C_4 products, formed in yields of about 30%, were consistently about one-half isobutene. Methylenecyclopropane is partially converted to the straight-chain butenes under the reaction conditions.

The high yields of 1,4-dimethylenecyclohexane and isobutene suggest the intermediacy of triplet-state trimethylenemethane. 1,4-Dimethylenecyclohexane is the expected product from the dimerization of two molecules of trimethylenemethane having opposite spins. Isobutene is also expected, being formed by abstraction of two hydrogen atoms from hydrocarbon or potassium hydride.

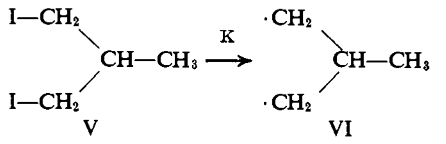






Methylenecyclopropane could result from (1) initial production of singlet trimethylenemethane or (2) ring closure of the triplet species with spin relaxation by contact with an alkali metal atom or a surface.

In contrast to the behavior of trimethylenemethane, the corresponding saturated diradical VI, formed from the reaction of 1,3-diiodo-2-methylpropane (V) with alkali metal vapor at 227–228°, gives methylcyclopropane, isobutene, and isobutane in yields of 76.7, 3.3, and 0.2%, respectively. 1,4-Dimethylcyclohexane or other products due to dimerization were not detected.



Extensive studies[10,11] of 1,2-, 1,3-, 1,4-, and 1,5-diradicals testify to the insignificance of bimolecular reactions, such as dimerization and disproportionations, in competition with unimolecular ring closure and rearrangement.

Although the reaction of 2-iodomethyl-3-iodopropene with alkali metal vapor is a two-step process, formation of 1,4-dimethylenecyclohexane cannot be due to the coupling of two monoiodo radicals. If this were the case, the saturated diiodide would also give dimeric material.[12] Hence, the preference for the bimolecular formation of 1,4-dimethylenecyclohexane and isobutene rather than the unimolecular formation of methylenecyclopropane is due to the greater stability, the greater reluctance to internal cyclization, and the longer lifetime of triplet trimethylenemethane relative to the saturated 1,3-diradical.

The failure to isolate the trimethylenemethane dimers by the pyrolysis[4] or photolysis[5] of 4-alkylidene-1-pyrazolines, or the pyrolysis of methylenecyclopropanes,[6] indicates that either the concentration of triplet trimethylenemethane was too low for bimolecular coupling to be observed or that triplet trimethylenemethane was not an intermediate in these reactions. Dimerization would be the expected reaction of the triplet molecule, formation of methylenecyclopropanes for the singlet. Theoretical considerations support these conclusions.[13]

Triplet tetramethylcyclobutadiene (VII) has been proposed as an intermediate in the reaction of *cis*-3,4-dichlorotetramethylcyclobutene and alkali metal vapor.[14] It would thus be expected that reaction of a mixture of this dichloride and 2-iodomethyl-3-iodopropene with alkali metal vapor would lead to the simultaneous production of triplet tetramethylcyclobutadiene (VII) and trimethylenemethane (II), which could then couple to produce 3-methylene-1,5,6,7-tetramethylbicyclo[3.2.0]heptene (VIII).[15] The experiment yielded, in addition to the expected products from the individual reactions of II and VII, a single cross-coupling product VIII, in 7% yield based on either reactant. This result suggests that both trimethylenemethane and tetramethylcyclobutadiene had the same electronic state, triplet. Had trimethylenemethane

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[8] The same products were obtained from 2-chloromethyl-3-chloropropene, but in lower yield. The dichloride was prepared by the method of B. C. Anderson, *J. Org. Chem.*, 27, 2720 (1962), and J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, 75, 3344 (1953).

[9] 1,4-Dimethylenecyclohexane was identified by comparison of the infrared spectrum and the melting point of its tetrabromide with those given in the literature [F. Lautenschlaeger and G. F. Wright, *Can. J. Chem.*, 41, 1972 (1963)]. The nmr spectrum had two singlets at 2.20 and 4.64 ppm in a respective ratio of 2:1.

[10] E. J. Goldstein, Ph.D. Thesis, The Pennsylvania State University, 1964; R. J. Petersen, Ph.D. Thesis, The Pennsylvania State University, 1964.

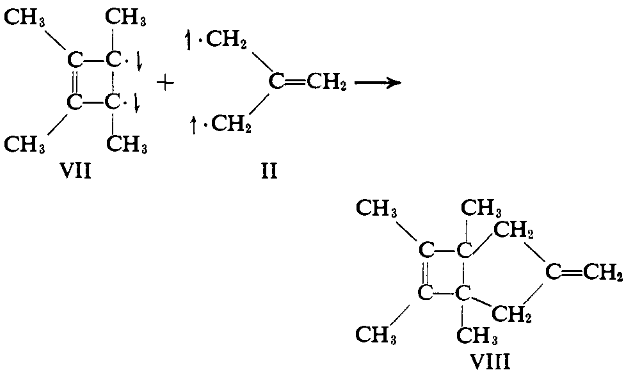
[11] R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **88**, 3963 (1966).

[12] Iodoalkanes react at nearly every collision with atomic sodium [E. Warhurst, *Quart. Rev.* (London), 5, 44 (1951)]. Since the iodine atoms in the precursor to trimethylenemethane are both allylic, they should react as fast or slightly faster than those in the saturated diiodide. Consequently, the rate of formation of trimethylenemethane is as great as or greater than the rate of formation of the saturated diradical.

[13] W. T. Borden, *Tetrahedron Letters*, 259 (1967).

[14] P. S. Skell and R. J. Petersen, *J. Am. Chem. Soc.*, **86**, 2530 (1964).

[15] The cross-coupling product VIII was identified on the basis of the following evidence: the mass spectrum had a parent peak at *m/e* 162 corresponding to the formula $C_{12}H_{18}$; the infrared spectrum showed absorbances at 5.91 (cyclobutene double bond), 7.28 (methyl group), 3.30, 6.00, and 11.35 μ (terminal methylene group); the nmr spectrum consisted of singlets at 1.02 and 1.41 ppm and multiplets centered at 2.00 and 4.64 ppm in ratio of 3:3:2:1, respectively.



VII II VIII

added to a singlet tetramethylcyclobutadiene, the resulting triplet adduct would not have been expected to give only a single cross-coupling product, but rather a number of monocyclic compounds *via* reduction, or internal or external disproportionation. Therefore the cross-coupling product VIII was formed in a one-step process involving the simultaneous formation of both bonds. The analogous bicyclic product[16] was obtained using *cis*-3,4-dichlorocyclobutene[17] and 2-chloromethyl-3-chloropropene, thus implicating a triplet cyclobutadiene intermediate.

The combined observations indicate that trimethylenemethane was produced and that is exists in a relatively stable triplet state, as predicted by theoretical calculations and in agreement with the esr results.

[16] 3-Methylenebicyclo[3.2.0]hept-6-ene was identified on the basis of the following spectral evidence: the mass spectrum had a parent peak at m/e 106 corresponding to the formula C_8H_{10}; the infrared spectrum showed absorption bands at 3.29 (vinyl hydrogen), 5.93 (cyclobutene double bond), 6.00, and 11.15 μ (terminal methylene group); the nmr spectrum consisted of a singlet at 5.91 ppm and multiplets at 4.83, 3.20, and 2.12 ppm in a ratio of 1:1:1:2, respectively.

[17] A generous sample of *cis*-3,4-dichlorocyclobutene was furnished by Professor C. D. Nenitzescu.

[18] This work was supported by the National Science Foundation.

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A Simple Floating Localized Orbital Model of Molecular Structure

Sir:

Most molecules have an even number of electrons which are generally paired off to create a ground state which is a spectroscopic singlet. For such molecules and states the following quantum mechanical model is proposed.

Let there be a minimal set of n floating localized orbitals φ_i which are, in general, nonorthogonal and real, and let each one be occupied by a pair of electrons with opposing spin. The $2n$-electron wave function can then be written as a single normalized Slater determinant

$$\psi = |\varphi_1(1)\bar{\varphi}_1(2)\varphi_2(3)\bar{\varphi}_2(4)\ldots\varphi_n(2n-1)\bar{\varphi}_n(2n)| \quad [1/(\sqrt{(2n)}!\ \det S)]$$

where the bars over certain orbitals indicate β spin as opposed to α for the others, and det S is the determinant of the orbital overlap matrix S with elements

$$S_{ij} = \int \varphi_i^* \varphi_j \, dv$$

Given the set of orbitals and the appropriate nonrelativistic Hamiltonian operator H, the mean energy E is calculated according to a formula adapted from one derived by Löwdin[1]

$$E = \int \psi^* H \psi \, d\tau = 2\sum_{i,j}(i/j)T_{ij} + \sum_{i,j,k,l}(ij/kl)(2T_{ij}T_{kl} - T_{il}T_{jk})$$

where

$$(i/j) = \int \varphi_i^* h \varphi_j \, dv$$

are the kinetic and potential energy integrals with the one-electron operator h, and

$$(ij/kl) = \int \varphi_i^*(1)\varphi_j(1)\varphi_k^*(2)\varphi_l(2)(1/r_{12}) \, dv(1)dv(2)$$

are the electron repulsion energy integrals. T_{ij}'s are elements of the reciprocal orbital overlap matrix

$$T = S^{-1}$$

For a given set of nuclear coordinates E is minimized, according to the variation method, by a variation in parameters defining the orbitals. This will generate a potential energy surface. If a "full minimization" of E with respect to nuclear coordinates as well as orbital parameters is carried out, then the equilibrium configurations of the molecule will be predicted. The calculation is strictly *ab initio* with no semiempirical parameters.

In this simple model the orbitals are taken to be floating spherical Gaussian functions[2]

$$\varphi_i = (2/\pi\rho_i^2)^{3/4} \exp[-(r_i/\rho_i)^2]$$

where r_i is the radial distance from the center of the orbital and ρ_i is an "orbital radius" parameter which defines a sphere which includes about 74% of the orbital charge density. For each orbital the coordinates of the center as well as the orbital radius are parameters to be varied.

Minimization of E with respect to all parameters will automatically lead to a result which will satisfy both the virial theorem and the Hellmann–Feynman theorem.[3]

Table I presents typical results for a series of diatomic and polyatomic molecules by the full minimization procedure.

The calculated energies are, of course, well above experimental values since no electron correlation is included other than that between electrons of like spin due to the antisymmetrization inherent in the determinantal wave function. Also the energies must be higher than those of Hartree–Fock calculations since the latter are by definition the values obtained by all possible variations of the orbitals in a single determinantal wave function. Because the total energies are crude, it would be expected that dissociation energies would be unsatisfactory and no attempt has been made to calculate them.

[1] P.-O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950).

[2] S. F. Boys, *Proc. Roy. Soc.* (London), **A200**, 542 (1950), introduction of gaussian orbitals; H. Preuss, *Z. Naturforsch.*, **11a**, 823 (1956); **19a**, 1335 (1964); **20a**, 18, 21, 1290 (1965); J. L. Whitten, *J. Chem. Phys.*, **39**, 349 (1963); **44**, 359 (1966); J. L. Whitten and L. C. Allen, *ibid.*, **43**, S170 (1965), use of off-center spherical Gaussian "pure" or "lobe" functions to simulate nonspherical atomic orbitals.

[3] A. C. Hurley, *Proc. Roy. Soc.* (London), **A226**, 170, 176, 193 (1954).