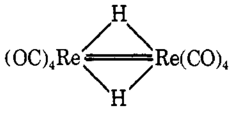
had been monochromated using an oriented graphite crystal.

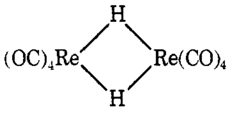
The structure has been solved from conventional Patterson and electron density maps using 1163 significant reflections ($I/\sigma(I) \geq 3.0$) collected in the range $0 < 2\theta < 41.5°$. Refinement of the structure by least squares was limited to the isotropic model in view of the obvious defects in the intensity data. This refinement has reduced the conventional R factor to 0.10. While the precision of the structure is low, the structural information on the $Re_2(CO)_8$ fragment is adequate for our purposes.

A view of the heavier atom skeleton is shown in Figure 1. Within experimental error, the structure had D_{2h} symmetry although this is not required crystallographically. The rhenium–rhenium distance of 2.90 Å is the shortest observed in a rhenium carbonyl cluster and may be compared with the hydrogen-bridged rhenium–rhenium distances of 3.17 Å in $[H_2Re_3(CO)_{12}^-]$,[8] 3.16 Å in $[H_6Re_4(CO)_{12}^{2-}]$,[9] and 3.295 (2) Å in $HRe_3(CO)_{14}$.[10] The two $Re(CO)_4$ fragments exhibit no significant angular deviations from those expected assuming that their structure is based on an octahedron (*i.e.*, all C–Re–C angles are either 90 or 180°) and all rhenium–carbon bond lengths are normal. The two hydrogen atoms would appear to be best placed in the plane defined by the rhenium atoms and the carbonyl groups labeled 2, 3, 6, and 7. This assumption is based on a consideration of intramolecular contacts and analogy to structures of the type $Mn_2(CO)_8Br_2$.[11] In view of their limited accuracy, one cannot infer from the structural results whether the hydrogen bridges are symmetrical or unsymmetrical. We assume the symmetrical structure for simplicity in the following discussion.

The effective atomic number rule at its simplest level would suggest that $H_2Re_2(CO)_8$ be formulated as **1**, with each hydrogen donating 0.5 electron to each rhenium and a double bond between the rhenium atoms. This highly formal description has the virtue of following precisely the electron bookkeeping system which requires no metal–metal bond in $[ClRe(CO)_4]_2$ and a single bond in $[Ph_2SiRe(CO)_4]_2$.[12]



1



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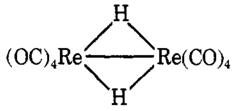

3

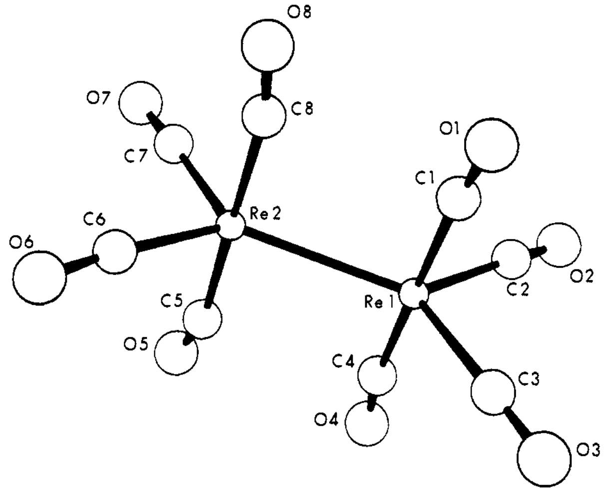

Figure 1. The molecular structure of $H_2Re_2(CO)_8$. Hydrogen atoms were not located and are not shown but are assumed to lie in the plane of carbonyl groups 2, 3, 6, and 7 in bridging positions between rhenium atoms. All C–Re–C angles are within two standard deviations of 90 or 180°. Average Re–C distance = 1.99 Å with typical individual standard deviation of 0.06 Å; Re–Re = 2.896(3) Å.

Alternatively, the H_2Re_2 bridge system (like that in B_2H_6[13]) could be considered, in an equivalent orbital context, to comprise a pair of three-center, two-electron bonds as in **2**, and this formulation too is consistent with the effective atomic number rule.[14] However, in this particular case, in view of the extremely short metal–metal distance, some degree of direct metal–metal interaction seems likely; in this regard, we offer structure **3**, by which we imply the sum of a two-electron, four-center H_2Re_2 bridge and a two-electron, two-center Re–Re bond. This approach, as well as the previous ones, can be considered to satisfy the effective atomic number rule, which is clearly of limited value in formulating the compound. A complete molecular orbital treatment of this bridged dimer would be most informative and probably essential in assessing the merits of representations such as **1**, **2**, and **3**.[15]

Acknowledgment. We thank the National Research Council of Canada for financial support and for scholarships to J. K. H. and W. L. H.

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(8) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Amer. Chem. Soc.*, **90**, 7135 (1968)

(9) H. D. Kaesz, B. Fontal, R. Bau, S. W. Kirtley, and M. R. Churchill, *ibid.*, **91**, 1021 (1969).

(10) Unpublished results of R. P. White, Jr., T. E. Block, and L. F. Dahl, cited by L. B. Handy, J. K. Ruff, and L. F. Dahl, *ibid.*, **92**, 7312 (1970).

(11) L. F. Dahl and C. H. Wei, *Acta Crystallogr.*, **16**, 611 (1963).

(12) This compound has been synthesized in our laboratory by Dr. J. K. Hoyano. The X-ray crystal structure done by Professor T. E. Haas shows idealized D_{2h} symmetry, with Re–Re = 3.00 Å and a Re–Si–Re angle of 75°.

(13) J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory," Wiley, New York, N. Y., 1965, Chapter 14.

(14) The manner of electron bookkeeping by which hydrogen-bridged metal carbonyl complexes are made to conform to the effective atomic number rule is outlined in detail by H. D. Kaesz, W. Fellmann, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, **87**, 2753 (1965).

(15) Positional parameters and bond distances and angles for $H_2Re_2(CO)_8$ will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-6232. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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A Molecular Orbital Model for the Photochemistry of β,γ-Unsaturated Ketones

Sir:

Intensive studies of the spectroscopic and photochemical behavior of β,γ-unsaturated ketones have led

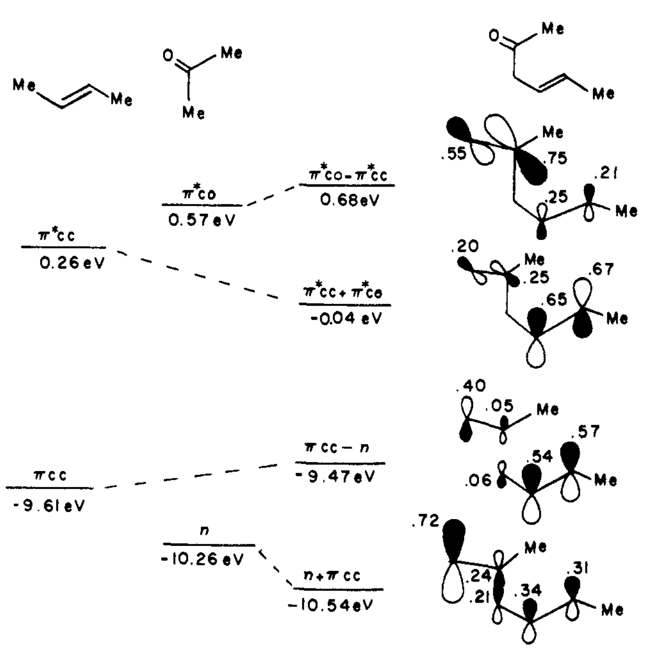
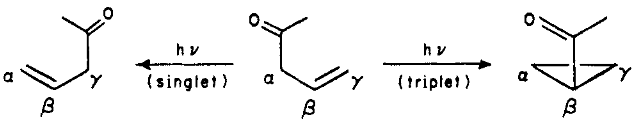


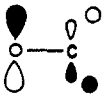
Figure 1. Calculated eigenvalues and eigenvectors for *trans*-2-butene, acetone, and *trans*-4-hexen-2-one.[8]

to the following generalizations: (1) enhanced n–π^* absorptions are observed when the carbonyl and alkene local planes have a dihedral angle near 90°,[1,2] (2) β,γ-unsaturated ketone singlets undergo [1,3] shifts faster than intersystem crossing;[2–4] (3) β,γ-unsaturated ketone triplets undergo oxa-di-π-methane rearrangements.[3]

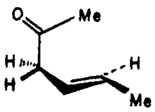


A possible explanation for the divergent behavior of β,γ-unsaturated ketone singlets and triplets has been proposed by Schuster, *et al.*[3b] These authors suggested that different spin density distributions in the excited singlet and triplet states lead to differing initial bonding interactions and, ultimately, to different products. These authors implicitly assumed that both excited singlets and triplets were n–π^* excited states. We wish to propose a different explanation based on differences in the electronic configurations of the excited singlets and triplets of these molecules.

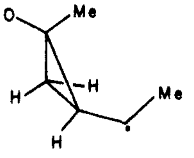
The two highest occupied and lowest vacant molecular orbitals for *trans*-4-hexen-2-one **1** are shown in Figure 1. The eigenvectors and eigenvalues have been obtained by the CNDO/S method parameterized by Jaffé and Del Bene.[7,8] This parameterization combined with configuration interaction between singly excited configurations yields reasonable transition energies and relative state energies. The molecular orbitals of **1** are those expected from mixing orbitals of *trans*-2-butene and acetone, and the orbital designations given in Figure 1 reflect the "origin" of the molecular orbitals of **1**. The n orbital is substantially delocalized in these calculations, as in other all valence electron calculations.[9] For example, the n orbital of formaldehyde may be represented by **2**.



2



1



3

After configuration interaction, the lowest excited singlet of **1** in the geometry shown is predicted to lie 3.27 eV above the ground state. Closely related com-

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(1) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956); H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959); A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, **84**, 1945 (1962); J. N. Murrell, "The Theory of Electronic Spectra of Organic Molecules," Wiley, New York, N. Y., 1963, pp 165–168; D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc. B*, 215 (1967); D. E. Bays and R. C. Cookson, *ibid.*, 226 (1967).

(2) J. R. Williams and G. M. Sarkisian, *Chem. Commun.*, 1564 (1971).

(3) Recent discussions and references: (a) R. S. Givens, W. F. Oettle, R. L. Coffin, and R. G. Carlson, *J. Amer. Chem. Soc.*, **93**, 3957 (1971); R. S. Givens and W. F. Oettle, *ibid.*, **93**, 3962 (1971); (b) D. I. Schuster, G. R. Underwood, and T. P. Knudsen, *ibid.*, **93**, 4304 (1971). Additional examples not referred to in part a or b: (c) H. Sato, N. Furutachi, and K. Nakanishi, *ibid.*, **94**, 2350 (1972); (d) N. Furutachi, Y. Nakadaira, and K. Nakanishi, *ibid.*, **91**, 1028 (1969); (e) N. Furutachi, J. Hayashi, H. Sato, and K. Nakanishi, *Tetrahedron Lett.*, 1061 (1972); (f) R. L. Cargill, M. E. Beckham, A. E. Siebert, and J. Dorn, *J. Org. Chem.*, 30, 3647 (1965); (g) G. R. Crow and K. C. Ramey, *Tetrahedron Lett.*, 3141 (1971); (h) M. Fischer and B. Zeek, *Chem. Ber.*, 101, 2360 (1968); (i) R. J. Chambers and B. A. Marples, *Tetrahedron Lett.*, 3747, 3751 (1971); (j) K. G. Hancock and R. O. Grider, *ibid.*, 4281 (1971); (k) J. R. Scheffer and R. A. Wostradowski, *ibid.*, 677 (1972).

(4) The only exceptions involve either 3-cyclohexenones, in which the C-1–C-2 bond is not favorably aligned for hyperconjugative interaction with the alkene π bond,[5] or β,γ-unsaturated ketones which are simultaneously α,β-unsaturated ketones so that intersystem crossing is facilitated.[6]

(5) J. R. Williams and A. Ziffer, *Tetrahedron*, **24**, 6725 (1968); J. Gloor, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **54**, 1864 (1971).

(6) P. A. Knott and J. M. Mellor, *Tetrahedron Lett.*, 1829 (1970); D. A. Plank and J. C. Floyd, *ibid.*, 4811 (1971).

(7) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807, 4050 (1968); **49**, 1221 (1968); **50**, 563 (1969). This method differs from the CNDO/2 method (J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970) mainly in the use of different parameterizations for the resonance integrals arising from σ or π overlap. Additional parameters are designed to reproduce spectral data, so that the ground-state calculations are generally less satisfactory than those by CNDO/2. For example, the orderings of n and π levels are not those deduced from photoelectron spectroscopy: D. Chadwick, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, **93**, 4320, 4962 (1971). Nevertheless, the parameterization and concomitant orbital energy ordering do lead to reasonable ground and first excited state separations after configuration interaction is included. Only *differences* in ground and excited states may reasonably be expected to result reliably from this method of calculation.

(8) The monoexcited states formed from these eigenvalues and eigenvectors form the basis set for a minimization of the lowest excited state energy through configuration interaction. The resulting excited state is a linear combination of monoexcited configurations. The coefficients next to each p orbital in Figure 1 are the resultant of vector addition of the $2p_x$, $2p_y$, and $2p_z$ atomic orbital coefficients on each atom. The positive lobe of each resultant orbital is indicated by shading. The calculations have been carried out for many different molecular geometries. Those calculations reported here were carried out for a geometry of the extended chromophores approximating that present in bicyclo[2.2.2]octenone (*cf.* **1**).

(9) L. Goodman and R. Zwarich, *J. Amer. Chem. Soc.*, **93**, 2068 (1971); J. M. Hollas, E. Gregorek, and L. Goodman, *J. Chem. Phys.*, **49**, 1745 (1968); R. Hoffmann and J. R. Swenson, *J. Phys. Chem.*, **74**, 415 (1970); N. W. Winter, T. H. Dunning, Jr., and J. H. Letcher, *J. Chem. Phys.*, **49**, 1871 (1968); J. R. Swenson and R. Hoffmann, *Helv. Chim. Acta*, **53**, 2331 (1970).

pounds have an enhanced n–π^* transition at 4.02 eV.[1] The lowest excited singlet state is composed primarily of n–π^* (n + $\pi_{CC} \rightarrow \pi^*_{CO} - \pi^*_{CC}$) (54%) and alkene–carbonyl charge transfer (π_{CC} − n $\rightarrow \pi^*_{CO} - \pi^*_{CC}$) (32%) configurations, in agreement with the traditional explanation of the enhancement of absorption of n–π^* transitions in β,γ-unsaturated ketones.[1]

The lowest triplet state calculated by this method is not an n–π^* state, but consists instead mainly of a π–π^* configuration (π_{CC} − n $\rightarrow \pi^*_{CC} + \pi^*_{CO}$) (76%). This state is predicted to lie 2.17 eV above the ground state. Although the calculated excited state energies are too low, the relative energetic ordering of states seems secure. For example, ^{1}n–π^* and ^{3}n–π^* states of simple ketones lie about 3.64 and 3.38 eV above the ground state, respectively, while $^1\pi$–π^* and $^3\pi$–π^* states of cyclic alkenes lie about 6 and 3.2 eV above the ground state, respectively.[10] Furthermore, phosphorescence from *trans*-5-hepten-2-one occurs from an alkene π–π^* triplet indicating that a disubstituted alkene triplet is lower in energy than a carbonyl ^{3}n–π^* state.[11]

These calculations provide a reasonable qualitative rationalization for the differing behavior of β,γ-unsaturated ketone singlets and triplets. By noting bond order differences between the ground state and an excited state, probable bonding changes in the excited state can be predicted.[12] Thus, the first excited singlet state (n–π^*) involves removal of an electron from a strongly α (C-2–C-3) bonding orbital and occupation of an orbital which has no α bonding and is weakly C-2–C-5 bonding, but C-2–C-4 antibonding. Clearly, α cleavage and/or C-2–C-5 bonding, leading ultimately to a 1,3-shift product, will be favored from the excited singlet state. The n–π^* triplet state is similar in configurational composition to the n–π^* singlet state and, due to neglect of differential overlap in this calculation, lies at 3.27 eV. Reactions from these two states should be similar.

By contrast, the lowest excited triplet state (π–π^*) involves little weakening of the α bond since mainly π_{CC}–n is vacated, and an electron fills an orbital which is C-2–C-4 bonding, but C-2–C-5 antibonding. Initial bonding changes in the triplet state would lead to diradical **3** as an intermediate or as one species on the concerted reaction surface. Another bonding change which is present in the triplet state is strong weakening of the π_{CC} bond. This bond order charge is much smaller in the excited singlet state. Thus, in addition to undergoing oxa-di-π-methane rearrangement, the triplet state might be expected to undergo cis,trans isomerization and, in cyclic cases, reactions characteristic of perpendicular or highly strained *trans*-cycloalkenes.

All of the experimental evidence obtained for a wide variety of β,γ-unsaturated ketones is compatible with this model. Thus, β,γ-unsaturated ketone singlets generally undergo [1,3] sigmatropic shifts, but α cleavages have been detected in a few cases.[3a,13,14] Closely related α-phenyl ketones undergo α cleavage from a ^{3}n–π^* state,[15] but these molecules should have a lowest n–π^* triplet since the triplet energy of benzene is about 3.65 eV.

β,γ-Unsaturated ketone triplets generally undergo the oxa-di-π-methane rearrangement, and, in some cases, other reactions characteristic of alkene π–π^* triplets such as intra-[14,16] or intermolecular[17] [2 + 2] cycloaddition, cis,trans isomerization,[18] and photoreduction.[17] In addition, phosphorescence from a rather long-lived (π–π^*) triplet has been observed with one β,γ-unsaturated ketone.[3j,11]

Further support for the validity of this rationalization may be found in our use of the Jaffé CNDO method to explain differences in 3,5-cycloheptadienone photochemistry resulting from subtle structural changes.[19] These kinds of arguments, which appear not to have been applied to nonplanar π systems previously,[20] may prove of more general applicability in considerations of photochemical reactivity.

Acknowledgment. Financial support by the Research Corporation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(10) N. J. Turro in "Energy Transfer and Organic Photochemistry," A. A. Lamola and N. J. Turro, Ed., Wiley-Interscience, New York, N. Y., 1969.

(11) S. R. Kurowsky and H. Morrison, *J. Amer. Chem. Soc.*, **94**, 507 (1972). After submission of this manuscript, phosphorescences from a number of β,γ-unsaturated ketones were reported: K. G. Hancock and R. O. Grider, *J. Chem. Soc., Chem. Commun.*, 580 (1972). The assignment of these phosphorescences to emission from π–π^* states based on relatively long triplet lifetimes (5.4–210 msec) is in complete accord with the calculations reported herein.

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(13) H. Morrison, *Tetrahedron Lett.*, 3653 (1964); J. Meinwald and P. J.-V. Vuuren, *Chem. Commun.*, 1460 (1971); P. S. Engel and H. Ziffer, *Tetrahedron Lett.*, 5181 (1969); J. E. Baldwin and S. M. Krueger, *J. Amer. Chem. Soc.*, **91**, 2396 (1969); D. I. Schuster, F.-T. H. Lee, A. Padwa, and P. G. Gassman, *J. Org. Chem.*, **30**, 2262 (1965); N. C. Yang and D. Thap, *Tetrahedron Lett.*, 3671 (1966).

(14) P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, **94**, 4357 (1972).

(15) K. Muller and G. L. Closs, *ibid.*, **94**, 1002 (1972); P. S. Engel, *ibid.*, **92**, 6074 (1970); W. K. Robbins and R. H. Eastham, *ibid.*, **92**, 6076 (1970).

(16) A. Shani, *Tetrahedron Lett.*, 569 (1972).

(17) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Amer. Chem. Soc.*, **88**, 1330 (1966).

(18) K. Takeda, I. Horibe, and H. Minato, *Chem. Commun.*, 87 (1971).

(19) K. N. Houk and D. J. Northington, *J. Amer. Chem. Soc.*, **94**, 1387 (1972).

(20) F. B. Tinland and C. Decoret, *Tetrahedron Lett.*, 3019 (1971).

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Intramolecular Thermal Cycloadditions of 1,8-Divinylnaphthalene and 1,8-Distyrylnaphthalene

Sir:

As an extension of our studies of the intramolecular photochemical cycloaddition reactions of 1,8-divinylnaphthalene (Ia) and *trans,trans*-1,8-distyrylnaphthalene (II),[1,2] we have examined the corresponding thermal ring closures of these compounds. Thermal [2 + 2] cycloadditions of simple olefins are not common,[3] and

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(1) J. Meinwald and J. W. Young, *J. Amer. Chem. Soc.*, **93**, 725 (1971).

(2) J. Meinwald, J. W. Young, E. J. Walsh, and A. Courtin, *Pure Appl. Chem.*, **24**, 509 (1970).

(3) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962); see also ref 4.

(4) S. F. Nelsen and J. P. Gillespie, *J. Amer. Chem. Soc.*, **94**, 6237 (1972).