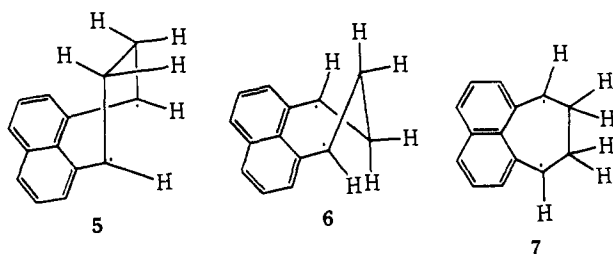


was determined that the detectable triplet was the excited state lying about 200 cal/mol above the singlet.

The same esr spectrum was observed when **1a** was irradiated in an ethanol glass at -160° . This is particularly exciting because, as seen in Table I, irradiation of **1b** in an ethanol glass at liquid nitrogen temperatures afforded the same products, **3** and **4**, and the same distribution of deuterium in **3** and **4**, as was observed in the thermal and photochemical decomposition in fluid solution. Thus, one can implicate a triplet state of the quinodimethane in the reaction sequence, at least in part.¹¹

2 is a highly flexible biradical. As a result of this inherent flexibility, it is not at all clear which conformation is responsible for the triplet signal and which conformation is responsible for the formation of products. Molecular models suggest that there are two stable conformations of **2**, one which is bent, **5** (C_s symmetry), and one which is twisted, **6** (C_i). To look into the questions raised above, we have carried out open shell INDO calculations¹²⁻¹⁴ on **5** and **6** as well as planar



7 (C_{2v}). The results of these calculations are shown in Table II.

As expected, the singlet (S) and triplet (T) electronic configurations of **7** are much less stable than the ground state configurations of **5** and **6**. This is what one would

(11) One cannot correlate the intensity of the triplet esr signal with the concentration of the biradical responsible for the signal. Consequently, it is conceivable that only a very small fraction of the reaction involves the triplet quinodimethane.

(12) Quantum Chemistry Exchange Program (Bloomington, Indiana), Program No. 141 by P. A. Dobosh described in detail in J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970. Known bond lengths of naphthalene and standard bond lengths of the remaining bonds were used.

(13) INDO calculations have previously been carried out on small open shell molecules. In these cases, the ordering of the singlet and triplet states is correctly predicted. In some instances the energy gap is somewhat large, though. See (a) R. N. Dixon, *Mol. Phys.*, **12**, 83 (1967); (b) J. A. Pople, D. C. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967); (c) the book cited in ref 12.

(14) INDO calculations of a similar vein have been carried out on the "parent" of **2**, i.e., tetramethylene. See L. M. Stephenson and T. A. Gibson, *J. Amer. Chem. Soc.*, **94**, 4599 (1972).

Table II. Calculated Binding Energies (au)

	5	6	7
Singlet	-14.246	-14.379	-14.146
Triplet	-14.323	-14.314	-14.246

expect intuitively due to the anticipated large angle strain of this molecule. It seems clear that **7** is not involved in the thermal or photochemical decomposition of **1**.

S-6 is seen to be lower in energy than T-6 and all other calculated geometries and multiplicities. Recall that the conclusion reached from the thermal and photochemical work was that the reactive intermediate was a ground state singlet or unquenchable triplet excited state. Thus, these calculations suggest that **3** and **4** are formed from the singlet twist conformation.

If **3** and **4** arise from a singlet twist conformation of **2**, what conformation of **2** yields the triplet esr? One cannot make any predictions from the calculations; in fact, a conformation other than those shown may be responsible for the esr.¹⁵ Perhaps the most interesting possibility is that one conformation is observed by esr while another goes directly to product, i.e., there may be more than one conformation of **2** on the reaction surface between the reactant and products.

In conclusion, it has been demonstrated that the same naphthoquinodimethane is generated thermally and photochemically, that a thermally accessible triplet also is an intermediate in the reaction, and, as inferred from the INDO calculations, the direct precursor to the products likely has a twist conformation and singlet multiplicity. Further efforts to define the nature of the 1,8-naphthoquinodimethane are in progress.

Acknowledgment. Appreciation is expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Research Corporation for the generous support of this research.

(15) A referee has suggested that because the radical centers in the bent conformation (**5**) overlap so strongly, the species which gives the esr signal resembles closely the naphthocyclobutane (**3**) in structure.

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Additions and Corrections

Stereochemistry and Mechanism of Acetolysis of 4,4-Dimethylcyclohexyl Tosylate [*J. Amer. Chem. Soc.*, **94**, 5133 (1972)]. By J. ERIC NORDLANDER* and THOMAS J. MCCRARY, JR., Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

The *E* configuration assigned to the minor solvolysis product, 3-methylcyclohexyl-3-methyl-*d*₃ acetate, **5**, is

incorrect; the proper assignment is *Z*. It was inferred correctly that the undeuterated methyl is that closer to the acetoxy group, but this position was mistakenly identified as *cis*. The substitution with hydride shift thus proceeds with *inversion* of configuration at the migration origin (and conforms with the results of ref li, j). The paper's principal conclusions, from the un-rearranged acetate, are not affected.

We thank Professor J. C. Richer for indicating the revision and communicating his complementary experimental results (with P. Bélanger, J. C. Florence, and A. Rossi).

Synthesis and Physical Properties of Barrelene, a Unique Möbius-like Molecule [*J. Amer. Chem. Soc.*, **91**, 2330 (1969)]. By HOWARD E. ZIMMERMAN,* GARY L. GRUNEWALD, ROBERT M. PAUFLER, and MAYNARD A. SHERWIN, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.

On page 2337 in the preparation 5,7-endo,endo-diaminobicyclo[2.2.2]-2-octene dihydrochloride, the "3.4 ml (0.190 mol) of 6 N hydrochloric acid" should read "34.0 ml (0.190 mol) of 6 N hydrochloric acid." Thus the number of moles of acid is correct but the volume given was in error, not giving enough to correspond to the 20.0 g (0.0892 mol) of dihydrazide reactant.

Nuclear Magnetic Resonance Studies of the Stereochemically Nonrigid Molecules B₆H₁₀, 2-CH₃B₆H₉, and 2-BrB₆H₉. Tautomerism of Bridging Hydrogens and the Influence of Substituents on the Position of the Basal Boron-Boron Bond in the Static Structures Observed at Low Temperature [*J. Amer. Chem. Soc.*, **95**, 6629 (1973)]. By V. T. BRICE, H. D. JOHNSON, II, and S. G. SHORE,* Evans Laboratory of Chemistry, The Ohio State University, Columbus, Ohio 43210.

In Table III the assignment for boron 2 at room temperature was omitted and that at -100° is incorrect. The correct values are -23.6 ppm at room temperature and -18 ppm at -100°.

Calorimetric and Equilibrium Studies on Some Stable Nitroxide and Iminoxy Radicals. Approximate O-H Bond Dissociation Energies in Hydroxylamines and Oximes [*J. Amer. Chem. Soc.*, **95**, 8610 (1973)]. By L. R. MAHONEY,* G. D. MENDENHALL, and K. U. INGOLD, Chemistry Department, Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121.

In the titles and column headings of Tables I and II and on page 8613, column 2, line 6, change **1** to **1a**. On

page 8613, column 1, line 3, change **1** and **1H** to **1a** and **1aH**. On page 8611, column 1, line 30, change "two more" to "the". In Table V, entry 6, final column, change 80.0 to 80.9. On page 8614, column 1, line 15, and footnote 33 change **1** to **1b**.

Chiral Recognition of Prochiral Centers. The (2S,9S)-2,9-Diamino-4,7-diazadecanecobalt(III) Mediated Decarboxylation of Aminoalkylmalonic Acids [*J. Amer. Chem. Soc.*, **96**, 809 (1974)]. By ROBERT C. JOB and THOMAS C. BRUCE,* Department of Chemistry, University of California, Santa Barbara, California 93106.

In the caption to Figure 4 the compound should be $\Delta(+)$ ₄₈₆- β -dinitro-2,9-diamino-4,7-diazadecanecobalt(III) perchlorate (**8b**). On page 814, column 2, line 9, change **8a** to **8b**.

1,1'-Azobisformamide. I. Photochemical Decomposition in Solution [*J. Amer. Chem. Soc.*, **96**, 1187 (1974)]. By RICHARD M. FANTAZIER* and JOHN E. HERWEH, Armstrong Cork Company, Research and Development Center, Lancaster, Pennsylvania 17604.

The Acknowledgment should read as follows: We wish to thank Dr. A. C. Poshkus for stimulating discussions involving the proposed decomposition path for ABFA, particularly those associated with the cyclic intermediate. We are grateful to Professor D. Swern, Temple University, for helpful suggestions in preparing the manuscript and to Mr. A. G. Geigley for recording the nmr spectra.

Formation of Mono- and Dianions of Polycyclic Hydrocarbons through Deprotonation with the Alkylolithium-N,N,N',N'-Tetramethylethylenediamine Complex. A Convenient General Method of Dehydrogenation [*J. Amer. Chem. Soc.*, **96**, 2434 (1974)]. By RONALD G. HARVEY* and HEE CHO, Ben May Laboratory, The University of Chicago, Chicago, Illinois 60637.

The following statement should be added to the Acknowledgment: Support of The University of Chicago Cancer Research Center Grant 1 PO1 CA 14599-01 is gratefully acknowledged.

Book Reviews*

Advances in Heterocyclic Chemistry. Volume 16. Edited by A. R. KATRITZKY and A. J. BOULTON (University of East Anglia). Academic Press, New York, N. Y. 1974. ix + 349 pp. \$35.00.

This volume contains three reviews on particular ring systems: 1,2,3-triazoles; nitrogen-bridged six-membered ring systems; and dibenzothiophenes. The literature has been surveyed to cut-off dates varying with the chapter from December, 1970, to mid-1972; it is most helpful to have this information clearly stated. Since these subjects have been reviewed before in one way or another, it is understandable that it is only recent developments that are the subjects of discussion.

There are also three other chapters, which deal with the general topics of base-catalyzed hydrogen exchange, homolytic substitution, and cationic polar cycloaddition. These are timely subjects.

* Unsigned book reviews are by the Book Review Editor.

The authors of the chapters are well chosen, and their chapters are informative and insofar as can be noticed, reliable and authoritative. As usual in this series, there is an author index, but not a subject index.

The Chemistry of Heterocyclic Compounds. Volume 28. Pyridazines. Edited by R. N. CASTLE (Brigham Young University). Wiley-Interscience, New York, N. Y. 1973. xii + 905 pp. \$80.00.

The impressive undertaking represented by this volume is to cover all the literature on pyridazines that was abstracted up to "mid-1971," and to list in tables all pyridazines known up to that time (condensed pyridazines appear in a companion volume). The task has been accomplished by the efforts of eight authors in nine chapters, the first of which is devoted to physical properties, and the rest to reactions and preparation of the various types of