

Figure 1. Idealized sketch of the $[\text{CeMo}_{12}\text{O}_{42}]^{3-}$ ion showing the linkage of the MoO_6 octahedra.

deviations from centrosymmetry, no indication of such deviations was seen, and space group $R\bar{3}$ was assumed and molybdenum positions were deduced from the map on that basis. (The cerium atom is at the unit cell origin.) After refinement of the molybdenum coordinates, a difference map gave the positions of the light atoms. The structure has now been refined by block-diagonal least squares, using isotropic thermal parameters, to a conventional R factor of 0.09. (The refinement is being continued using anisotropic thermal parameters.) The successful refinement appears to confirm the choice of space group. Programs used were those written for the IBM 360 system by Ahmed, *et al.*¹¹

The anion consists of six Mo_2O_9 units formed by two octahedra sharing a face. The Mo_2O_9 units share corners with each of four adjacent Mo_2O_9 units to build up the anion (see Figure 1). Two corners are on the shared face and the other two are the innermost ones opposite the shared face. Mo–O distances presently have estimated standard deviations of 0.01 Å and vary from 1.68 to 2.28 Å. The Mo–O bond lengths fall into three classes, 1.68 Å (unshared oxygen atoms), 2.28 Å (shared-face oxygen atoms involved in corner-sharing), 1.98 Å (the oxygen atom in the shared face, not involved in corner sharing and the inner oxygen atoms involved in corner sharing). The lengths can be correlated with the number of heavy atoms with which an oxygen atom is associated, the shortest lengths being those corresponding to oxygen atoms associated with only one molybdenum atom. This variation of length with the number of heavy atoms with which an oxygen atom is associated, and resultant displacement of the molybdenum atoms toward the outside of the anion, was first noted by Keggin² and again by Yannoni⁶ and Evans⁷ and was confirmed by Perloff³ in a more accurate study. The 12 molybdenum atoms form a slightly distorted icosahedron around the central cerium atom.

The cerium atom is 12-coordinate and the coordination polyhedron is an icosahedron formed by two shared-face oxygen atoms from each of the six Mo_2O_9 units. The two independent Ce–O distances are both 2.50 Å with an estimated standard deviation of 0.01 Å. This distance may be compared with the average Ce–O distance of 2.51 Å in the icosahedrally coordinated cerium atom

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in ceric ammonium nitrate as reported by Beineke and Del Gaudio.¹² The cerium coordination polyhedron, in the present work, is not a completely regular icosahedron (only 3 symmetry is required by the space group), but deviations from regularity are fairly small. The angles in the triangular faces, for example, vary from 57.2 to 61.7° with estimated standard deviations of 0.3°.

The water molecules and ammonium ions appear to fill the space between the anions and to connect the structure in a hydrogen-bonded network.

Acknowledgment. This investigation was supported by PHS Training Grant No. DE159 of the National Institute of Dental Research.

(12) T. A. Beineke and S. Del Gaudio, Paper M11, presented before the American Crystallographic Association Meeting, Minneapolis, Minn., 1967.

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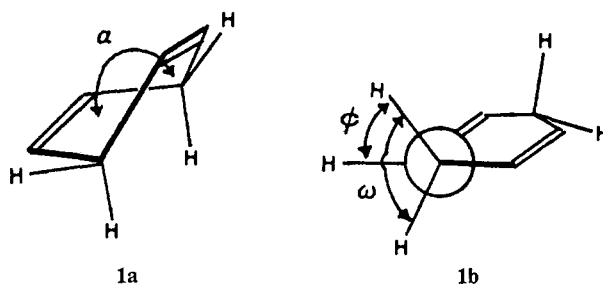
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The Conformation of 1,4-Cyclohexadiene from Stereoisomeric Allylic–Allylic Proton Couplings

Sir:

It has been nearly 20 years since Gerding and Haak¹ deduced from vibrational spectral analyses that 1,4-cyclohexadiene (**1**) is planar (D_{2h}) or nearly so. Yet, unexplainably, **1** is regarded generally to occupy the boat (C_{2v}) conformation.² Recent analyses of the vibrational^{3a} and rotational^{3b} spectra of **1** confirm the original conclusions of Gerding and Haak, and Hendrickson-type calculations give a shallow potential minimum for the D_{2h} conformation.⁴ We present here additional evidence for the near-planar conformation of **1**.



Should the five-bond allylic–allylic proton couplings in **1** be dominated by σ – π interaction contributions, then the present theory for such interactions⁵ leads to eq 1,

$$J_c/J_t = \{(\sin^2 \phi)^2 + [\sin^2(\omega - \phi)]^2\} / 2(\sin^2 \phi) \times [\sin^2(\omega - \phi)] \quad (1)$$

(1) H. Gerding and F. A. Haak, *Rec. Trav. Chim.*, **68**, 293 (1949).

(2) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 125.

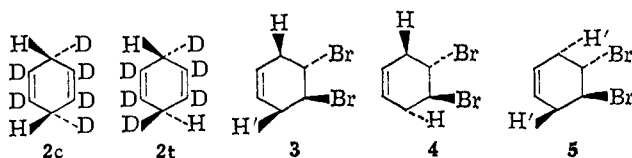
(3) (a) H. D. Stidham, *Spectrochim. Acta*, **21**, 23 (1965); (b) B. J. Monostori and A. Weber, *J. Mol. Spectry.*, **12**, 129 (1964).

(4) The calculations were performed using normal bond lengths, the torsional potential function of propene, a C–C–C bending force constant of 17.5 cal mol⁻¹ deg⁻², and 122 and 112° for the normal equilibrium bond angles for the C=C–C and C–C–C fragments, respectively. The assistance of Carol M. Sprecher in carrying out these calculations is gratefully acknowledged.

(5) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

where J_c and J_t are couplings between the *cis* and *trans* allylic hydrogens in **1** and ϕ and ω are the angles shown in **1b**. Equation 1 predicts that $J_c = J_t$ for planar **1** and that, in general, $J_c/J_t \geq 1$ for all angles ϕ .

We have determined the magnitudes of J_c and J_t in the following way. The Birch reduction of hexadeuteriobenzene proceeded without isotopic disarray to give a mixture of **2c** and **2t**. The pmr spectrum⁶ of **2** shows a single resonance at τ 7.44 ppm. The low-field ¹³C-H satellite spectrum ($J_{^{13}\text{C-H}} = 126.0$ cps) of the allylic hydrogens of **2** is shown in Figure 1a. There, the frequency separations between the two inside and two outside absorptions (8.04 ± 0.01 and 9.63 ± 0.03 cps, respectively) correspond to the two allylic-allylic proton couplings.⁷ The reduction is nonstereoselective, as the areas of these two pairs of transitions are equal within experimental detection.



Bromination of **2** in chloroform at 0° gave a mixture of stereoisomeric dibromides **3**, **4**, and **5**, the pmr spectrum⁶ of which (in CCl_4) is shown in Figure 1c. The nonequivalent *cis* hydrogens of **3** give rise to an AB spectrum; $J = 2.40 \pm 0.04$ cps, $\tau_{\text{H}_3} = 6.859 \pm 0.008$, and $\tau_{\text{H}'_3} = 7.476 \pm 0.008$ ppm. Both **4** and **5** contain equivalent *trans* hydrogens having τ values of 6.856 ± 0.005 and 7.477 ± 0.004 ppm, respectively. Integration of the absorptions in Figure 1c gives $[3] = 2[4] = 2[5]$.

The labeling of the absorptions as shown in Figure 1c becomes clear after enriching the stereoisomeric mixture of dibromides with **5** by selective removal of **3** and **4** through dehydrobromination (to benzene product) using potassium *t*-butoxide in *t*-butyl alcohol. Dibromide **5** has only deuterium *trans* to bromine, but **3** and **4** have at least one *trans* hydrogen and bromine. Thus, realization of a normal primary kinetic isotope effect⁸ (i.e., $k_{\text{H}}/k_{\text{D}} \simeq 6$) in the elimination of the first hydrogen bromide molecule should bring about a substantial enrichment in **5** after several reaction half-lives. Carrying the dehydrobromination to about 80% completion led to a mixture of unreacted dibromides consisting of 23, 2, and 75% of **3**, **4**, and **5**, respectively, as determined from its pmr spectrum (Figure 1d). Debromination of these residual dibromides using zinc and acetic acid-ether gave a mixture of 23% of **2c** and 77% of **2t**, the ¹³C-H satellite spectrum of which is shown in Figure 1b.

The stereoisomeric allylic-allylic proton couplings in **1** thus have been unambiguously characterized and determined to be $J_c = 9.63$ and $J_t = 8.04$ cps.

The experimental value of 1.20 for J_c/J_t fulfills the requirement of eq 1 that this ratio be ≥ 1 . If ω is taken to be 120° , eq 1 gives $\phi \simeq 45^\circ$ (or 75°), and so α (see **1a** where $\alpha \cong 180^\circ - \frac{1}{2}(60^\circ - \phi)$) is about 172° .

(6) All nmr spectra were determined on a Varian A-60 instrument and under conditions of deuterium decoupling.

(7) The ¹³C-H satellite spectra of isotopically unsubstituted **1** gave by inspection ($J_c + J_t$) = 17.6 ± 0.5 cps and $J(\text{vinyl-vinyl}) = 10.0 \pm 0.5$ cps. As expected, J_c and J_t are of the same sign.

(8) See, for example, W. H. Saunders, Jr., and D. H. Edison, *J. Am. Chem. Soc.*, **82**, 138 (1960).

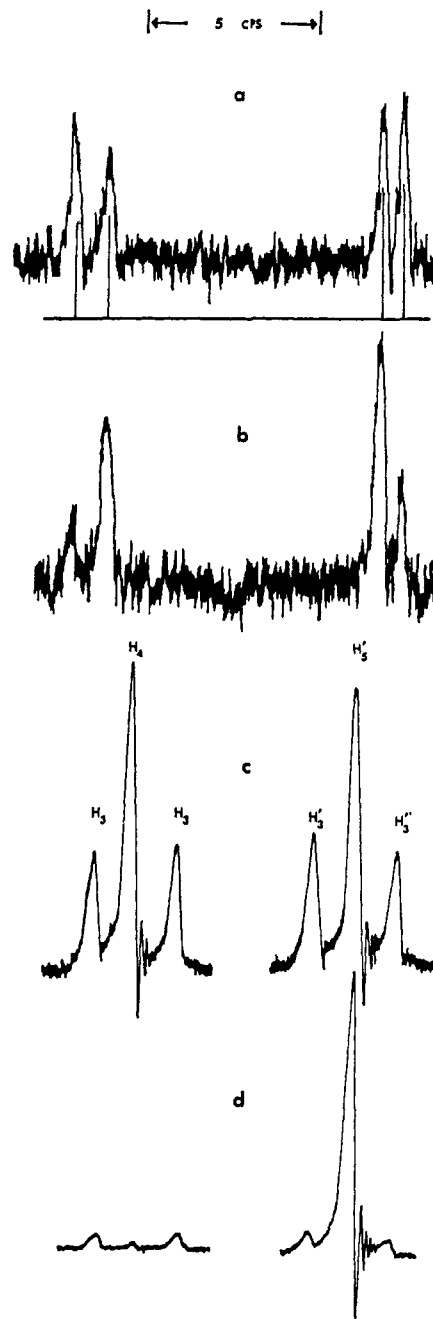


Figure 1. (a) Low-field ¹³C-H satellite pmr spectrum⁶ of a 1:1 mixture of **2t** and **2c**. The "stick spectrum" is that calculated taking $J_{^{13}\text{C-H}_1} = 126.0$ cps and $J_{^{13}\text{C-H}_4} = 0$ cps for both the *cis* and *trans* hydrogens. (b) Low-field ¹³C-H satellite pmr spectrum of a 77:23 mixture of **2t** and **2c**. (c) Pmr spectrum⁶ of a 2:1:1 mixture of **3**, **4**, and **5**. (d) Pmr spectrum⁶ of a 23:2:75 mixture of **3**, **4**, and **5**.

Using this estimated value of ϕ and the average energy approximation,⁵ calculated values of J_c and J_t are 8.8 and 7.3 cps, respectively. The near-coplanarity of **1** as estimated by this approach agrees favorably with the conclusions mentioned earlier.^{1,3,4}

Present knowledge of allylic-allylic proton couplings is insufficient to estimate the reliability of the molecular parameters derived from the approach described here. Particularly, we note that eq 1 was derived from a six-electron (four σ and two π) localized $\text{HCC}=\text{C}$ fragment model⁵ (**1** is composed of four such fragments). To

what extent the use of more complete molecular wave functions would alter the numerical values of J_c/J_t derived from eq 1 is unknown. Such a treatment, however, may preclude the equivalency of J_c and J_t in planar 1 (i.e., when $\omega = 2\phi$). Also, indirect σ -electron contributions to five-bond allylic-allylic couplings generally may not be negligible.

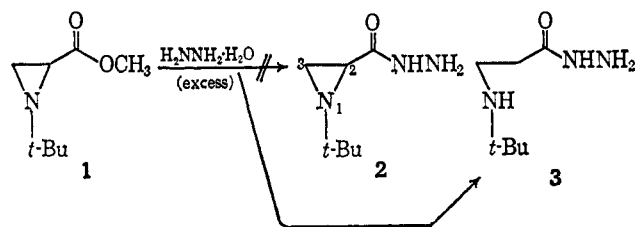
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Diimide Formation via an Aziridine Rearrangement

Sir:

An attempt to prepare N-*t*-butylaziridine-2-carboxylic acid hydrazide (2) according to standard procedures¹ from ester 1² and excess hydrazine hydrate at room temperature (4 days) or at reflux (5 hr in ethanol) resulted in copious gas evolution. The sole organic product of the reaction was identified as hydrazide 3.³ This



ring-opening reduction was neither expected nor with apparent precedent and thus prompted further investigation.

A solution of 1 (1.1 molar excess) and hydrazine hydrate was allowed to stand at room temperature for 9.5 hr. Analysis of the resultant mixture (in D₂O) by nmr spectroscopy revealed the formation of methanol as well as a slight change in the pattern and chemical shift of the characteristic three-proton aziridine ring multiplet. Although its instability precluded isolation, we assign structure 2, the originally expected hydrazide, to the product. In a similar manner, the N-benzyl analog 4⁴ could be prepared and isolated as a spectrally pure, crystalline precipitate (66%). Formation and identification of products 2 and 4 thus rule out any form of direct reductive ring scission by hydrazine.⁵

Characteristic reactions of 2 and 4 are shown in Scheme I. In each case cleavage occurred at both the N₁-C and CO-N bonds. Diimide 9 and amino ketene 10 constitute possible products of such cleavage. The

(1) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 273.

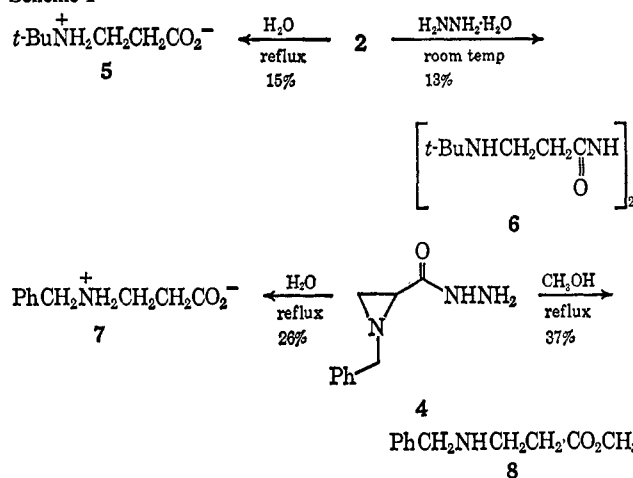
(2) Prepared by a procedure similar to that of M. A. Stolberg, J. J. O'Neill, and T. Wagner-Jauregg, *J. Am. Chem. Soc.*, **75**, 5045 (1953); C. L. Moyer, unpublished results.

(3) This compound was characterized by microanalysis and by ir, nmr, and mass spectroscopy.

(4) This compound was characterized by nmr, ir, and mass spectroscopy. It was also converted to a stable acetone hydrazone.³

(5) In agreement with this hypothesis is the observation that representative aziridines, e.g., N-*t*-butyl-2-aziridinecarbinol and 1,2-diphenylaziridine, were stable to hydrazine hydrate in methanol at room temperature.

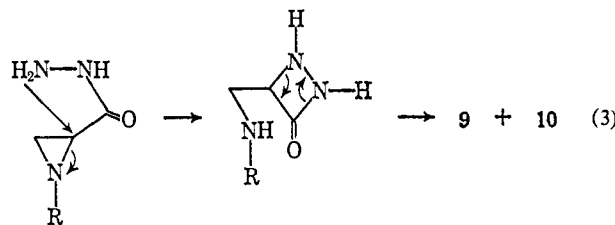
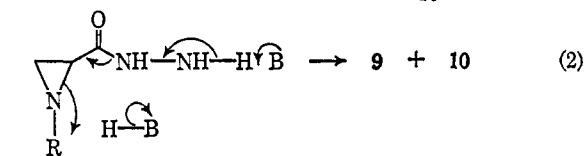
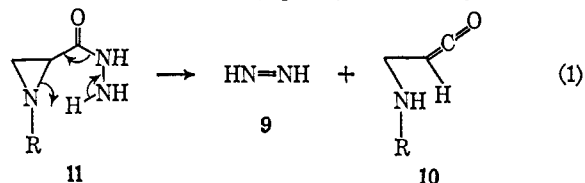
Scheme I



former would account for the observed gas evolution and the latter for products 3, 5,³ 6,⁶ 7,⁷ and 8.⁸ Confirmatory evidence for the intermediacy of diimide was, in fact, obtained from the observation of concurrent reduction of azobenzene to hydrazobenzene in the conversion of 4 to 8.⁹ Based on the above evidence, a



number of alternative formulations for this rearrangement may be considered¹⁰ (eq 1-3). Although we can-



not distinguish between paths 1 and 2, path 3 appears unlikely in view of the known and predicted behavior of 1,2-diazetidone-3-ones¹¹ as well as the known course of intramolecular nucleophilic epoxide and aziridine ring opening.

(6) Compound 6³ crystallized from an attempted preparation of 2 in which equimolar amounts of 1 and hydrazine hydrate were used. It apparently is formed from the reaction of 3 with 10.

(7) This compound was identical with an authentic sample: A. Zilkha, E. S. Rachman, and J. Rivlin, *J. Org. Chem.*, **26**, 376 (1961).

(8) The hydrochloride of 8 was identical with an authentic sample: P. L. Southwick and R. T. Crouch, *J. Am. Chem. Soc.*, **75**, 3413 (1953).

(9) The reduction was followed by tlc. Hydrazobenzene was recovered from the reaction mixture and shown to be identical with that prepared by the method of E. J. Corey, W. L. Mock, and D. J. Pasto, *Tetrahedron Letters*, 347 (1961).

(10) These formulations are not intended to imply any necessarily concerted timing in the events leading from 11 to the products. A mechanism similar to (2) has been postulated for the formation of diimide and ketenes from the reactions of mono-, di-, and trichloroacetyl hydrazide hydrochlorides with base: R. Buyle, *Helv. Chim. Acta*, **47**, 2449 (1964).

(11) L. Horner and E. Spietschka, *Chem. Ber.*, **89**, 2765 (1956).