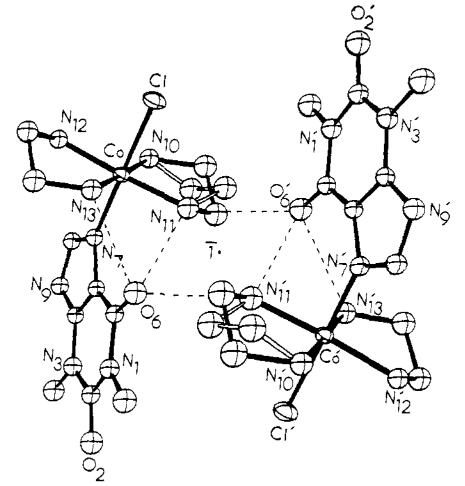

Figure 1. A perspective view of the molecular conformation of the complex *trans*-[Co(en)$_2$Cl(C$_7$H$_7$N$_4$O$_2$)]$^+$. The two complex ions shown are symmetry related by the center of inversion at ($^1/_2$, 0, $^1/_2$).

adenine complex,[5] the coordination to cobalt was through N-9, and N-3 was found to be hydrogen bonded to the ethylenediamine groups (displayed in a cis conformation about the cobalt). Several important features appear immediately on comparison of the two complexes: (1) the N-3–N-11, N-3–N-13 intramolecular hydrogen bond system in the adenine complex has been supplanted by the O-6–N-11, O-6–N-13 intramolecular hydrogen bond system in the theophylline complex; (2) the angles C-5–N-7–Co, 132.0°, and C-8–N-7–Co, 124.9°, are highly dissymmetric. The analogous angles in the adenine complex are C-4–N-9–Co, 127.7°, and C-8–N-9–Co, 128.4°. This dissymmetry in the theophylline complex is unusual for metal–purine[6] or metal–imidazole[7] complexes. The asymmetry is obviously a result of molecular adjustment in order to accommodate the enlargement of the intramolecular hydrogen ring system from a five-membered ring in the adenine complex to a six-membered ring in the theophylline complex. The important feature is that the noted angles have been significantly altered in order to form the intramolecular hydrogen bond system. The particulars of the intermolecular and intramolecular hydrogen bonding are illustrated in Figure 2.

The hydrogen bonding of the carbonyl group, C-6–O-6, of the theophylline to the ligated ethylenediamines is specific for the guanine class of bases. Reaction of the complex with an adenine residue *via* N-7 would cause severe steric repulsion between the ethylenediamine ligands and the amino group at C-6. This suggests then that selectivity for guanine over adenine residues may be achieved by using octahedral complexes with *hydrogen donor ligands* attached.

Furthermore, reaction of the complex with a biopolymer may be achieved without severe disruption of intermolecular purine–pyrimidine hydrogen bonding. The Watson–Crick hydrogen bonding scheme[8] for G:C pairs has been recently confirmed at atomic resolution for the dinucleoside phosphate guanylyl-3′,5′-cytidine.[9]

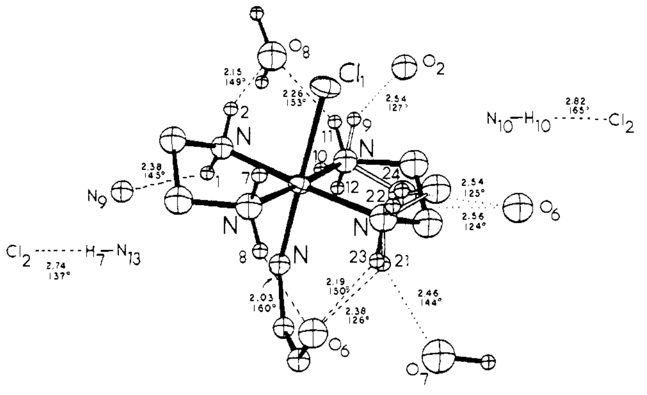

Figure 2. A perspective view showing some of the intramolecular and intermolecular hydrogen bonds stabilizing the molecular conformation of the complex. Hydrogen bonds are indicated by dashed lines; interatomic contacts are indicated by dotted lines.

The carbonyl oxygen O-6 of guanine is involved in an intermolecular hydrogen bond with the amino group N-4 of the cytidine base. Coordination of the complex at N-7 could result in two possibilities: (1) rupture of the O-6$_G$–N-4$_C$ hydrogen bond and formation of an O-6$_G$–N(ethylenediamine) hydrogen bond; (2) O-6 acting as a bifurcated acceptor between N-4$_C$ and N-(ethylenediamine). In either case the other two hydrogen bonds of the G:C pair could remain intact.

Acknowledgments. The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Institutes of Health (Biomedical Science Support Grant) for support of this work through grants to L. G. M. and T. J. K. The diffraction equipment was purchased through a grant from the National Science Foundation.

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Received July 30, 1973

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(6) M. Sundaralingam and J. A. Carrabine, *J. Mol. Biol.*, **61**, 287 (1971).

(7) H. C. Freeman, *Advan. Protein Chem.*, 22, 257 (1967).

(8) J. D. Watson and F. H. C. Crick, *Nature* (*London*), **171**, 737 (1953).

(9) R. D. Day, N. C. Seeman, J. W. Rosenberg, and A. Rich, *Proc. Nat. Acad. Sci. U. S.*, 70, 849 (1973).

The [2.2.2]Propellane System[1,2]

Sir:

We report now the first synthesis, isolation and characterization of a [2.2.2]propellane. Our successful synthesis of this elusive system is outlined in Chart I. The route to the diazo ketone **1** shown there is described in more detail in our earlier communication on the synthesis of [4.2.2]- and [3.2.2]propellanes.[3] Photolysis of **1** at −70° in methylene chloride gave the ketene **2**.[4] The reaction was monitored by infrared spectroscopy, following the disappearance of the carbonyl band of **1** at 6.12 μ. The ketene was not isolated but was cleaved directly to ketone **3** by ozonolysis at −70° in 2:1 by

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[1] A preliminary report of this work was presented at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973.

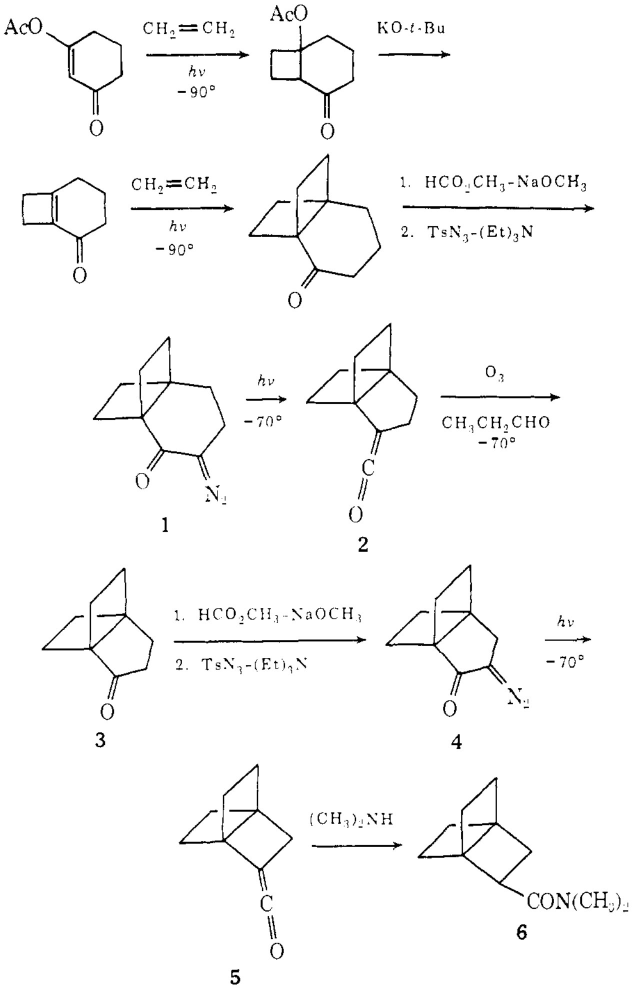
[2] The proper name for the skeleton in the Baeyer system is tricyclo[2.2.2.0^{1,4}]octane. For an excellent review of recent propellane chemistry see D. Ginsburg, *Accounts Chem. Res.*, **5**, 249 (1972).

[3] P. E. Eaton and K. Nyi, *J. Amer. Chem. Soc.*, **93**, 2786 (1971).

[4] For other examples of photochemical Wolff reactions see ref 3, footnote 8 therein, and A. Hassner, A. W. Coulter, and W. S. Seese, *Tetrahedron Lett.*, 759 (1962).

volume methylene chloride–propionaldehyde;[5] **3**, bp 55–57° (1 Torr), was isolated in 45% yield overall from **1**. Conversion of **4** to the corresponding diazo ketone **4**, mp 87.8–88.2°, *via* the intermediate α-formyl compound was straightforward and could be carried out in 83% yield.[6] Ultraviolet irradiation of diazo ketone **4** in 1:3 by volume methylene chloride–dimethylamine produced the [2.2.2]propellane **6** by way of the ketene **5**.[7] Work-up by chromatography on silica gel at −30° permitted isolation of the pure, crystalline, colorless propellane amide in 40% yield from **4**. The 270-MHz nmr spectrum of **6** is reproduced in Figure 1a.

Chart I



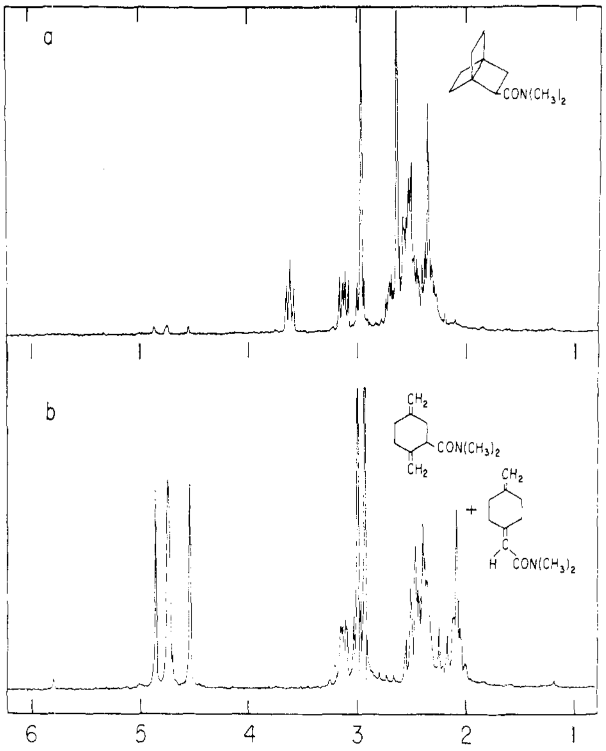
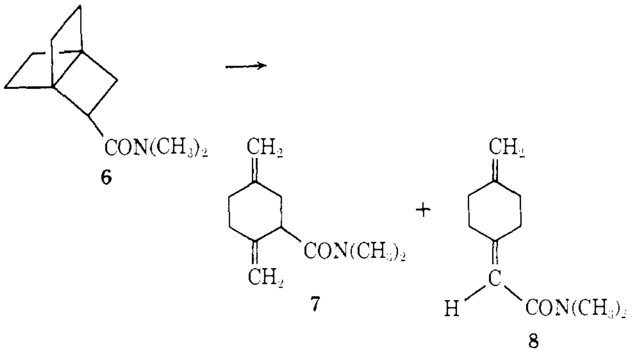


Figure 1. The 270-MHz spectra of (a) propellane amide **6** and (b) the mixture of unsaturated amides **7** and **8** produced upon thermal opening of **6**. The scale is in parts per million downfield from internal tetramethylsilane. The spectra were taken on solutions of equal concentration in $CDCl_3$ at −30°. The solution of **6** stood for several hours at −30° before spectrum 1a was recorded; signals from the decomposition product **7** are just visible.

The very strained [2.2.2]propellane amide is unstable thermally as expected. In solution in deuteriochloroform it undergoes first-order ring opening to a mixture (~9:1) of the unsaturated, monocyclic amides **7** and **8**.



The half-time for opening to **7** at 25° is about 28 min, $k_1 \simeq 4 \times 10^{-4}$ sec^{-1}. Figure 1b is the 270-MHz nmr spectrum of a solution of **6** like that used to obtain the spectrum in Figure 1a but warmed to 45° for 20 min. Insofar as can be determined by nmr, the conversion $\mathbf{6} \rightarrow \mathbf{7} + \mathbf{8}$ is clean. The activation energy for the process is ~22 kcal/mol, as determined by a standard rate study over the temperature range +7 to +35°.[8]

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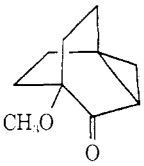
[5] The yield is very poor in the absence of propionaldehyde. We chose to run the reaction in the presence of the aldehyde after studying the work on ozonization of P. R. Story, J. A. Alford, J. R. Burgess, and W. C. Ray, *J. Amer. Chem. Soc.*, **93**, 3042, 3044 (1971).

[6] We used a slight modification of the general procedure of M. Rosenberger, P. Yates, J. B. Hendrickson, and W. Wolf, *Tetrahedron Lett.*, 2285 (1964); see M. Regitz and J. Rüter, *Chem. Ber.*, **101**, 1263 (1968).

[7] Irradiation of **4** in methanol gives the expected [2.2.2]propellane ester along with the cyclopropane ketone illustrated. We have shown



that this cyclopropane results from acid-catalyzed, thermal reaction of methanol with the ketene **5**. Similar products are *not* observed on photolysis of other closely related propellane diazo ketones.[3] We are exploring this matter in detail.

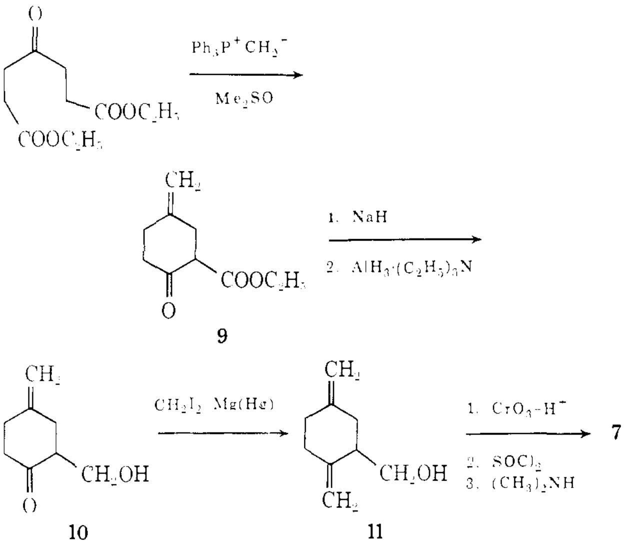
[8] Concerted $2_s + 2_s$ fragmentation of **6** is clearly symmetry forbidden. Stohrer and Hoffmann[9] and Newton and Shulman[10] have considered theoretically a two-step opening process for the parent propellane. Our experimental results and the theoretical work are in rough accord.

[9] W. D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 779 (1972).

[10] M. D. Newton and J. M. Schulman, *J. Amer. Chem. Soc.*, **94**, 4391 (1972).

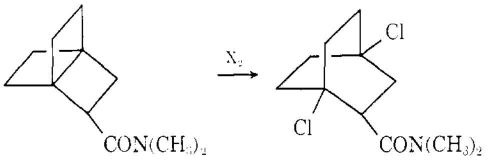
The structure of the minor product **8** from the ring opening of **6** was deduced from the compound's origin and the spectral data: ir (CCl_4) ν 1635, 892 cm^{-1}; nmr (CCl_4, 270 MHz) δ 5.71 (1 H, s), 4.64 (2 H, 4-Hz apart), 3.00 (3 H, s), 2.88 (3 H, s), 2.52 (2 H, t, J = 6 Hz), 2.24 ppm (6 H, br s). The structure of **7** was arrived at similarly (see Figure 1b) and was confirmed by unambiguous synthesis of the compound (Chart II).

Chart II



Reaction of diethyl γ-ketopimelate (Aldrich) with an excess of methylenetriphenylphosphorane in Me_2SO provided for the introduction of an exocyclic methylene group and subsequent Dieckmann condensation to the carboethoxycyclohexanone **9** in 60% yield, bp 59–60° (1 Torr). Rapid salt formation from the β-keto ester interfered with further methylenation under basic conditions. Treatment[11] of the sodium enolate of **9** in glyme with aluminum hydride–triethylamine in benzene led to reduction of the ester group alone and gave the hydroxymethyl ketone **10** in 50% yield, bp 58–60° (20 mTorr). This compound could be methylenated satisfactorily (70%) with methylene iodide–magnesium amalgam[12] giving the diene **11**, which was taken on without complete purification. Adjustment of oxidation state and subsequent production of the requisite amide were done as illustrated and need no further comment. The final product was shown to be identical spectroscopically and chromatographically with the amide **7** formed from thermal cleavage of the propellane **6**.

The [2.2.2]propellane **6** reacts very rapidly with chlorine to give **12**, mp 121.5–122.5°, the product of addition across the central bond. The structure of **12** was confirmed by an independent, unambiguous synthesis of the compound. Diels–Alder reaction of 1,2,3,4-tetrachloro-1,3-cyclohexadiene with excess acryloyl chloride at 140° for 3 days gave a mixture of adducts that was taken directly to the corresponding mixture of dimethylamides (72% overall; 5 parts endo, mp 196–197°; 1 part exo, mp 110.5–111.5°). Reduction of these, together or alone, with hydrogen over palladium-on-carbon in methanolic sodium hydroxide gave **12** in excellent yield. The propellane **6** reacts instantly with bromine at −70° to give the dibromo adduct **13**, mp 117–118°. No doubt these reactions reflect $sp^{<3}$ hybridization of the tetrasubstituted bridgehead atoms (taken on to meet the structural demands of the carbon skeleton), a weak central bond formed to a significant degree by σ overlap of p orbitals, and the great strain inherent in the [2.2.2]propellane system.[13]



6

12, X = Cl
13, X = Br

Acknowledgments. Generous support of this work by the National Science Foundation is recognized with thanks. We are grateful to Dr. J. C. Kauer of Du Pont for a sizable sample of tetrachlorocyclohexadiene.

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[11] The method follows from a suggestion in N. M. Yoon and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 2927 (1968). The reagent was purchased from Lithium Corporation of America.

[12] G. Cainelli, F. Bertini, P. Grasselli, and G. Zubiani, *Tetrahedron Lett.*, 5153 (1967).

[13] The [2.2.2]propellane **6** does not react with oxygen at a noticeable rate. This is quite unlike the much less strained propellanes 1,3-dehydroadamantane[14] and [3.2.1]propellane[15] which copolymerize with oxygen extremely readily. These contain a cyclopropane unit.

[14] R. E. Pincock, J. Schmidt, W. B. Scott, and E. J. Toruka, *Can. J. Chem.*, **50**, 3958 (1972).

[15] K. B. Wiberg and G. J. Burgmaier, *J. Amer. Chem. Soc.*, **94**, 7396 (1972).

[16] Shell Research Foundation Predoctoral Fellow.

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Triboluminescence of Hexaphenylcarbodiphosphorane. Emission from a Molecular Excited State Populated by Mechanical Stress

Sir:

The phenomenon of triboluminescence, the emission of light caused by application of mechanical stress to crystals, has been known since the 17th century.[1] Although a wide variety of organic and inorganic crystals are triboluminescent,[2] the specific mechanisms of the excitation and the excited-state origins of the emission are not known for most of the crystals studied.[3] In some cases, the emissions originate from triboelectrification[4] of the solid. Evidence for an electrical mechanism was provided by the observation that the triboluminescence of *cis*-4-octene in an atmosphere of neon exhibited the red glow of an electrical discharge in that gas.[5] The triboluminescence of zinc sulfide crystals has been attributed[3] to an electroluminescent mechanism on the basis of the correspondence between the electro- and triboluminescence spectra. In this communication we report the triboluminescence spectrum

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[1] G. Wiedemann and F. Schmidt, *Ann. Phys. Chem.*, **54**, 606 (1895). Triboluminescence was first named in this reference. It takes its prefix from the Greek "tribein," to rub.

[2] G. Wolff, G. Gross, and I. N. Stranske, *Z. Elektrochem.*, **56**, 420 (1952).

[3] P. A. Thiessen and K. Meyer, *Naturwissenschaften*, **57**, 423 (1970).

[4] S. DePaoli and O. P. Strausz, *Can. J. Chem.*, **48**, 3756 (1970).

[5] M. C. Hoff and C. E. Boord, *J. Amer. Chem. Soc.*, **72**, 2770 (1950).