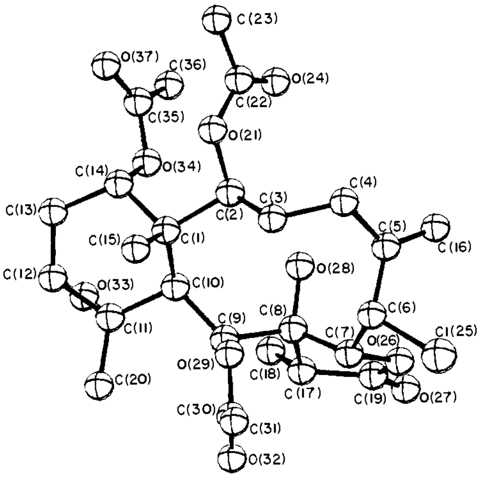


**Figure 1.** A computer-generated perspective drawing of **1**. Hydrogens are not shown, and no absolute stereochemistry is implied.

The structure factors were converted to normalized structure factors and phases were assigned by a multisolution, weighted tangent formula approach.[4] All nonhydrogen atoms were located in successive electron density syntheses and hydrogens in a final difference electron density synthesis. Full-matrix least-squares refinements with anisotropic temperature factors for nonhydrogen atoms and isotropic temperature factors for hydrogen have converged to a final crystallographic residual of 0.046 for the observed reflections.[5] Additional crystallographic details can be found in the supplemental material; see paragraph at end of paper.

Figure 1 is a perspective drawing of the final x-ray model of stylatulide. All bond distances generally agree well with accepted values. The intra-ring bond angles in the ten-membered ring are all larger than normal tetrahedral angles. This presumably is a consequence of relief of steric strains across the ring. There are short contacts between O(28)-C(2) of 2.89 Å, C(9)-C(2) of 3.28 Å, and C(8)-C(5) of 3.21 Å. The torsional angles around the ten-membered ring range widely, but there exists an approximate twofold axis which bisects the C(1)-C(10) and C(5)-C(6) bonds. The $\gamma$-lactone ring has an envelope conformation with C(8) serving as the flap. Since the torsional angles about the C(11)-C(12) and C(12)-C(13) bonds are essentially 0, the cyclohexane ring has a 1,2-diplanar conformation. There are no intermolecular contacts less than the van der Waals distance, save one C—OH···O=C distance of 2.93 Å.

Although chlorine-containing diterpenes were known to exist for more than 10 years,[6] the structures have been slow to appear. The structures of the "briareins", metabolites of the gorgonian coral *Briareum asbestinum* have recently been determined.[7] Briarein-A, whose structure was also determined by x-ray analysis,[8] has the same ring system with a similar substitution pattern. The structure of the toxin from the sea pen *Ptilosarcus gurneyi* (or *P. quadrangularis*)[9] is also related to stylatulide (**1**) and briarein-A.[10] In the copepodite assay, stylatulide (**1**) was toxic ($LD_{100}$) at concentrations greater than 0.5 ppm.

**Acknowledgments.** The copepodite assay was performed by Ms. M. S. Wolfe in our laboratory. Comparison of the voucher sample with materials in the SIO invertebrate collection was carried out by S. Luke. Collections of *Stylatula* were made during a cruise of R/V Dolphin funded by the National Science Foundation (BMS75-07659). S.J.W. wishes to thank the National Science Foundation for a graduate fellowship.

**Supplementary Material Available:** Fractional coordinates (Table 1), bond distances (Table 2), bond angles (Table 3), and observed and calculated structure factors (Table 4) (14 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) The alcyonarians of the Gulf of California have not been studied in detail. A preliminary examination showed that the voucher sample resembled *Stylatula elongata*, a species found along the California coast. For a key to alcyonarians from the California coast, see C. Hand, in "Light's Manual: Intertidal Invertebrates of the Central California Coast", R. I. Smith and J. T. Carlton, Ed., U.C. Press, Berkeley, 1975.
(2) M. J. Cormier, K. Hori, Y. D. Karkhanis, J. M. Anderson, J. E. Wampler, J. G. Morin, and J. W. Hastings, *J. Cell. Physiol.* **81**, 291 (1973).
(3) A satisfactory elemental analysis was obtained.
(4) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
(5) The following library of crystallographic programs was used: C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFT and FRIEDEL", USAEC Report IS-2625, Iowa State University, Institute for Atomic Research, Ames, Iowa, 1971; W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least Squares Program", USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965; C. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program", USAEC Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(6) R. W. Hyde, Ph.D. Dissertation, University of Oklahoma, Norman, 1966.
(7) L. S. Ciereszko, personal communication; C. Bartholome, doctoral dissertation, Universite Libre de Bruxelles, 1974.
(8) J. E. Burks, D. van der Helm, C. Y. Chang, and L. S. Ciereszko, *Acta Crystallogr.*, in press.
(9) J. C. Wekell, Proceedings, 4th Food-Drugs from the Sea Conference, Marine Technology Society, in press.
(10) S. J. Wratten, W. Fenical, D. J. Faulkner, and J. C. Wekell, unpublished results.
(11) Camille and Henry Dreyfus Foundation Teacher–Scholar Grant Awardee 1972–1977.

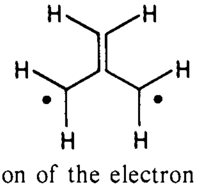
**Stephen J. Wratten, D. John Faulkner***
*Scripps Institution of Oceanography*
*University of California, San Diego*
*La Jolla, California 92093*

**Ken Hirotsu, Jon Clardy***[11]
*Ames Laboratory—USERDA and Department of Chemistry*
*Iowa State University, Ames, Iowa 50011*
*Received January 11, 1977*

## Trimethylenemethane. A Reversible, Temperature Dependent Transformation from Higher to Lower Symmetry as Observed by Electron Spin Resonance Spectroscopy

*Sir:*

Trimethylenemethane[1a] (I), in its ground triplet state,[1b] is characterized by a four-line electron spin resonance spectrum.[2] The presence of four lines, rather than six, is a consequence of the $D_{3h}$ symmetry[1b] of the triplet I. In this, and in other instances of threefold or higher symmetry, the molecular $x$ and $y$ axes[3] are equivalent and the lines corresponding to them coincide forming a pair of $xy$ lines, for instance, the inner two lines in the spectrum of trimethylenemethane-$d_6$ (I-$d_6$) in Figure 1a. In molecules of lower symmetry, $C_{2v}$ for example, the $xy$ lines are split into their component $x$ and $y$ lines giving rise to four inner lines,[2-4] instead of two. The outer two lines in the spectrum of Figure 1a are the $z$ lines;[2-4] their presence is not dependent upon the molecular symmetry.



I
I-$d_6$, H=D

Examination of the electron spin resonance spectrum of trimethylenemethane-$d_6$ (I-$d_6$) has revealed an extremely facile apparent interconversion of states of different symmetry of the triplet I. Thus, irradiation of methylenecyclopropane-$d_6$[5] with $\gamma$-rays,[7] at the boiling point of liquid nitrogen, gives rise to the spectrum of the triplet state of trimethylenemethane-$d_6$ (I-$d_6$) shown in Figure 1a. As the temperature is raised from

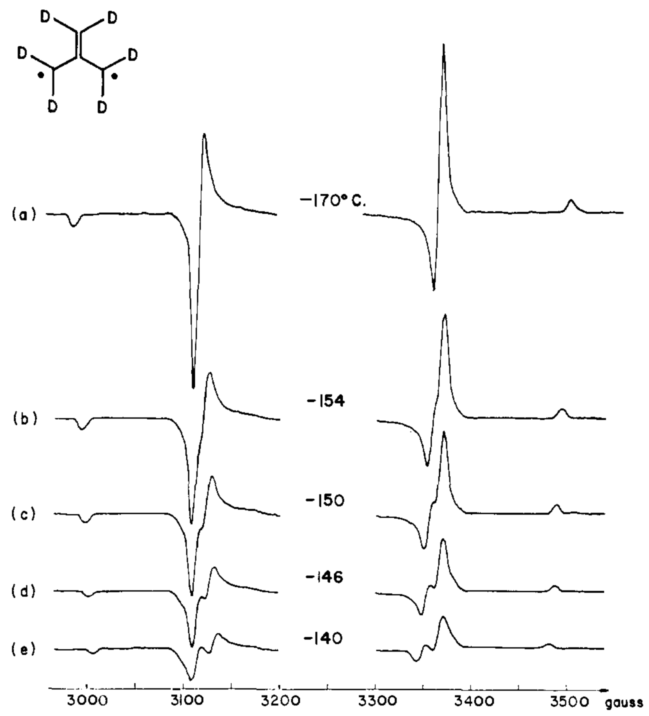


**Figure 1.** Electron spin resonance spectrum of trimethylenemethane-$d_6$, from $\gamma$-radiolysis of neat methylenecyclopropane-$d_6$, showing the change in the $xy$ and $z$ lines as a function of temperature.

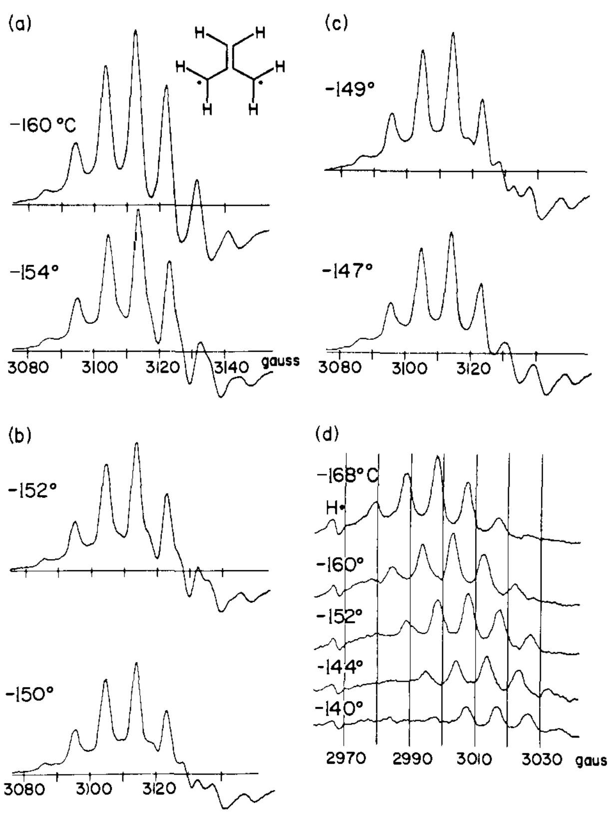


**Figure 2.** Electron spin resonance spectrum of trimethylenemethane, from $\gamma$-radiolysis of neat methylenecyclopropane, showing: (a–c) the variation in shape of the low-field $xy$ line as a function of temperature; (d) movement toward the center of the spectrum and absence of change in shape for the low-field $z$ line. The small peak at 2968 G is due to the hydrogen atom. It is a convenient reference point for the movement of the $z$ line.

−196 °C, the lines of the spectrum broaden[8] and the $z$ lines move toward the center of the spectrum. At −155 °C a more startling change begins to occur in the $xy$ lines. A shoulder appears which continues to develop as the temperature is increased, until at −140 °C the $xy$ lines become clear doublets. The course of the change in the spectrum is shown in Figures 1a–e.

The splitting of the $xy$ lines is reversible. The original unsplit spectrum is restored when the sample is cooled to temperatures below −155 °C.[9]

The splitting of the $xy$ lines is not dependent on the presence of deuterium. Examination of the parent undeuterated triplet I, from $\gamma$-radiolysis of methylenecyclopropane,[7] over the critical temperature region (−155 to −140 °C), again reveals the development of reversible new splitting in the $xy$ lines, as shown in Figures 2a–c. In experiments described very recently,[7c] Yoshida and Edlund report that the hyperfine splitting of the $xy$ lines of the triplet I exhibits no significant dependence on temperature. The reported experiments[7c] did not, however, encompass a careful examination of the spectra in the critical temperature region between −160 and −140 °C.

Observation of the temperature dependent splitting depends critically on the degree of resolution of the electron spin resonance spectrum. Thus, the spectrum obtained by photolysis of 3-methylenecyclobutanone[11] in randomly oriented frozen matrices is not sufficiently well resolved to allow the observation of the temperature dependent splitting of the $xy$ lines. The latter spectra do show, however, a reversible decrease in $D$ value with increasing temperature,[8] which appears (vide infra) to have the same origin as the reversible splitting of the $xy$ lines.

Two general explanations for the splitting of the $xy$ lines may be advanced. There may exist, under the conditions of temperature employed, only one electronic state of trimethylenemethane (I), the $D_{3h}$ triplet ground state, but there may be two or more magnetically nonequivalent sites provided by the matrix. The magnetic distinctions among the different sites would be required to be a function of temperature. Alternatively, there may exist a second electronic state of trimethylenemethane (I), energetically accessible and of symmetry lower than $D_{3h}$, such that the second state becomes populated as the temperature is raised.

The latter interpretation appears, on the basis of the observed spectra, to be the more acceptable of the two possibilities. Did there exist magnetically nonequivalent sites in the matrix, giving rise to multiple $xy$ lines, then the $z$ lines of the triplet spectrum must also be split in identical fashion.[12] No such splitting of the $z$ lines is discernible in the spectrum of either the deuterated (Figure 1) or nondeuterated (Figure 2d) trimethylenemethanes (I). Additional support for this position is derived from examination of the triplet spectrum of trimethylenemethane-$d_6$ (I-$d_6$) in matrices other than neat methylenecyclopropane-$d_6$. The same temperature dependent splitting of the $xy$ lines is observed in the spectra obtained from samples prepared by $\gamma$-irradiation of solutions of methylenecyclopropane-$d_6$ in hexafluorobenzene (25, 12, and 5%, wt/wt, solutions) and in tetrahydrofuran (ca. 50% solution).[13]

The available evidence being indicative of a minimal effect of the matrix on the splitting of the $xy$ lines, the tentative hypothesis may be advanced that the splitting results from the intervention of a second electronic state of trimethylenemethane (I). As noted above, the second state must become populated as the temperature is raised and be characterized by symmetry lower than that of the parent $D_{3h}$ ground state triplet of I. The argument is strengthened by the fit of the spectra observed, at the several temperatures of Figure 1, to a Hamiltonian.[4] For example the spectrum obtained at −140 °C can be fitted to a Hamiltonian[4,12,14] with $D = 0.0219$ and $E = 0.0054$ cm$^{-1}$. It is a consequence of the appearance of the new component to the $xy$ line that the center of gravity of that line moves toward the center of the spectrum, as shown in

Figure 1. Such a shift results in a decrease in the magnitude of $D$.[8,12] In order that the spectrum continue to fit a Hamiltonian, the separation between the $z$ lines must decrease in a parallel fashion. Figures 1 and 2d show very clearly the decreasing separation between the $z$ lines as the temperature is raised.[15]

What is the nature of the new state of trimethylenemethane? Theoretical estimates[16] of the difference in energy between the planar (0,0,0) and perpendicular (0,0,90) triplet trimethylenemethanes (I) range from 8[16a] and 10[16b] to approximately 17[16c,d,e] kcal/mol. It may be argued that even the lowest of these values is too great to account satisfactorily for a transformation in which it appears that rapid equilibration or averaging occurs near −150 °C. While the theoretical results can in no way alone be taken to rule out the (0,0,90) form as a possibility, they do encourage a search for alternative possible states of the triplet (I) which might be accessible under the conditions of the experiments described above.

In their recent theoretical examination of trimethylenemethane (I), Yarkony and Schaefer[13c] noted that when the $^3A_2'$ ground state of trimethylenemethane was described as the $^3B_2$ state of $C_{2v}$ symmetry, the energy was not changed.[17] No further discussion of the $^3B_2$ state has occurred and there have been no predictions that it might represent a stable minimum on any reaction pathway of the triplet I. It is intriguing to speculate, however, that the temperature dependent splitting of the $xy$ lines might be the result of the reversible interconversion of the $^3B_2$ and $^3A_2'$ states. Such an averaging between states of $D_{3h}$ and $C_{2v}$ symmetry would provide an explanation for the observed temperature dependent splitting. It would also lead to an understanding of the decrease in the $D$ value. Thus, if the molecule is transformed from $D_{3h}$ to $C_{2v}$ symmetry by way of an $E'$ vibration, this would entail not only contraction of the central bond angle but also lengthening of the opposing carbon–carbon bond.[18] The net effect would be an increased average separation between the two unpaired electrons and a consequent decrease in the value of $D$.[12] However, it is not intuitively obvious and it is correspondingly unsettling, that what appears to be a normal vibrational mode, the contraction of the bond angle at the central carbon atom of I, should lead to a potential minimum. *If* so, this symmetry-breaking step would add a bizarre new dimension to the chemical and spectroscopic attributes of trimethylenemethane (I).[19]

**Acknowledgment.** This work was generously supported by the National Science Foundation (NSF Grant No. MPA74-07864). It is a pleasure to acknowledge stimulating conversations with Professor William Doering and Dr. David Dixon of Harvard University and with Dr. Hueiming Chow of Case Western Reserve University.

## References and Notes

(1) (a) P. Dowd, *Acc. Chem. Res.*, **5**, 242 (1972); J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremmeling, *J. Am. Chem. Soc.*, **93**, 1544 (1971); (b) M. S. Platz, J. M. McBride, R. D. Little, J. J. Harrison, A. Shaw, S. E. Potter, and J. A. Berson, *ibid.*, **98**, 5725 (1976); R. J. Baseman, D. W. Pratt, M. Chow, and P. Dowd, *ibid.*, **98**, 5726 (1976). In the present paper we assume that the ground state of the triplet I has $D_{3h}$ symmetry, recognizing that, although this assumption is in full accord with current theoretical expectation and with the observation that the zero field splitting parameter $E = 0$, the precise spatial symmetry of the triplet I remains to be established by experiment.

(2) The four lines are the $\Delta m = 1$ lines appearing at 2993, 3118, 3368, and 3502 G at −175 °C. There is, of course, a fifth line in the spectrum, the $\Delta m = 2$ line at 1618 G, which is not shown in any of the figures. The latter peak is relatively little changed in appearance over the temperature range examined in the present study.

(3) The $x$ and $y$ axes are taken to be those lying in the horizontal plane of the molecule; the $z$ axis is that normal to the horizontal plane. For each one of the Cartesian coordinates $x$, $y$, and $z$, two $\Delta m = 1$ lines are generated, giving rise, when the three axes are distinct from one another, to a total of six lines.[4]

(4) W. A. Yager, E. Wasserman, and R. M. R. Cramer, *J. Chem. Phys.*, **37**, 1148 (1962).

(5) Prepared by condensation of acetaldehyde-$d_4$ (more readily available than acetaldehyde-1-$d_1$) with formaldehyde-$d_2$ yielding pentaerythritol-$d_8$. The latter was then converted to methylenecyclopropane-$d_6$ by published procedures.[6] The isotopic purity of the methylenecyclopropane-$d_6$ was high; the final product contained 96% $C_4D_6$ and 4% $C_4HD_5$.

(6) A Mooradian and J. B. Cloke, *J. Am. Chem. Soc.*, **67**, 942 (1945); J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *ibid.*, **75**, 3344 (1953); B. C. Anderson, *J. Org. Chem.*, **27**, 2720 (1962).

(7) (a) K. Takeda, H. Yoshida, K. Hayashi, and S. Okamura, *Bull. Inst. Chem. Res. Kyoto Unit.*, **45**, 55 (1967); (b) T. Yamaguchi, M. Irie, and H. Yoshida, *Chem. Lett.*, 975 (1973); (c) H. Yoshida and O. Edlund, *Chem. Phys. Lett.*, **42**, 107 (1976).

(8) Over the temperature range −196 to −155 °C, the $xy$ lines in the spectrum of I-$d_6$ broaden from 9 to 17 G and the $z$ lines move toward the center of the spectrum by approximately 10 G.

(9) The temperature range over which the splitting occurs is that in which trimethylenemethane (i) closes to methylenecyclopropane at a measurable rate.[10] Lowering the temperature restores the original spectrum, with the $xy$-lines unsplit, but it is accompanied by some loss in intensity due to the ring-closure reaction. Even with the loss in intensity in the higher temperature reaches, it is still possible to demonstrate many reversible cycles of the splitting in the $xy$ lines. When the triplet spectrum described above (Figure 1) is allowed to decay completely, there remains a very weak apparently more stable (less reactive) triplet spectrum ($D = 0.025$, $E = 0$ cm$^{-1}$) which differs from that described above in being almost completely unresponsive to temperature. This observation will be described in more detail shortly.[10]

(10) P. Dowd and M. Chow, to be submitted for publication.

(11) P. Dowd and K. Sachdev, *J. Am. Chem. Soc.*, **89**, 715 (1967).

(12) Stated more fully: in the spectrum of an $n$-fold symmetric triplet ($n \geq 3$), the separation between the $xy$ lines is a characteristic of the triplet called the zero-field parameter $D$. Ordinarily expressed in units of wavenumbers (cm$^{-1}$), the $D$ value is generally taken as a measure of the magnitude of the dipolar interaction between the unpaired electrons. The $D$ value for trimethylenemethane (I) is 0.025 cm$^{-1}$ at 196 °C. For all randomly oriented triplet molecules, the separation between the two $z$ lines is required to be $2D$. Thus, a splitting of the $xy$ lines, if it is the result of site nonequivalence reflected in the $D$ value, must also be manifested by splitting, to the same extent, of the $z$ lines.

(13) In hexafluorobenzene the spectra were weaker than those obtained from samples of neat methylenecyclopropane-$d_6$, and the effect of changing the matrix is to decrease somewhat the stability of the diradical I-$d_6$ in the critical temperature region.

(14) The zero-field parameter $E$ is obtained from the triplet spectrum and is one-third of the separation between the $x$ and $y$ lines. $E$ is generally taken as a measure of the asymmetry of the triplet molecule, being zero for molecules in which the $x$ axis is equivalent to the $y$ axis (threefold or higher symmetry axis) and taking on nonzero values for molecules in which the $x$ axis is not equivalent to the $y$ axis.

(15) All of the samples examined, including those in hexafluorobenzene and tetrahydrofuran, and those prepared starting with 3-methylenecyclobutanone showed the same temperature dependent variation in the $D$ value as that shown in Figures 1 and 2b. The decrease in the $D$ value has also been noted recently by others,[7c] and the change ascribed, on the basis of no other evidence, to molecular out-of-plane vibrations.

(16) (a) M. J. S. Dewar and J. S. Wasson, *J. Am. Chem. Soc.*, **93**, 3081 (1971); (b) J. Olsen and S. Kang, *J. Mol. Struct.*, **9**, 315 (1971); (c) D. R. Yarkony and H. F. Schaefer, *J. Am. Chem. Soc.*, **96**, 3754 (1974); (d) W. Hehre, L. Salem, and M. Wilcott, *ibid.*, **96**, 4328 (1974); (e) J. H. Davis and W. A. Goddard, *ibid.*, **98**, 303 (1976).

(17) Although explicit point was not made of it, the state diagrams of Davis and Goddard[16e] and of W. T. Borden, *Tetrahedron Lett.*, 259 (1967), carry the implication that the $^3A_2'$ and $^3B_2$ states should be considered to be close in energy.

(18) F. A. Cotton, "Chemical Applications of Group Theory", 2nd ed, Wiley, New York, N.Y., p 297.

(19) A referee has suggested that the temperature dependent splitting of the $xy$ lines might arise through wide amplitude torsional motion of the methylene groups. He has proposed that such a motion in the E mode will confer an average $C_{2v}$ geometry on the ($D_{3h}$) ground state. The referee prefers this explanation because it neither requires a new electronic state which is almost degenerate with the ground state nor two potential minima associated with the same normal mode. While we cannot rule out such an explanation, the proposal that one electronic state (the $D_{3h}$ ground state) can take on an average $C_{2v}$ character through one torsional mode seems most unusual. It ignores the other 23 vibrational modes and makes tenuous the idea that discrete molecular electronic states can be classified and characterized according to a single average symmetry.

**Paul Dowd,* Mudan Chow**
*Department of Chemistry, University of Pittsburgh*
*Pittsburgh, Pennsylvania 15260*

*Received October 27, 1976*

---

## Synthesis and Crystal Structure of *cis*-Diammineplatinum α-Pyridone Blue

*Sir:*

The blue compounds formed from aqueous solutions of platinum(II) in the presence of amides have been a subject of