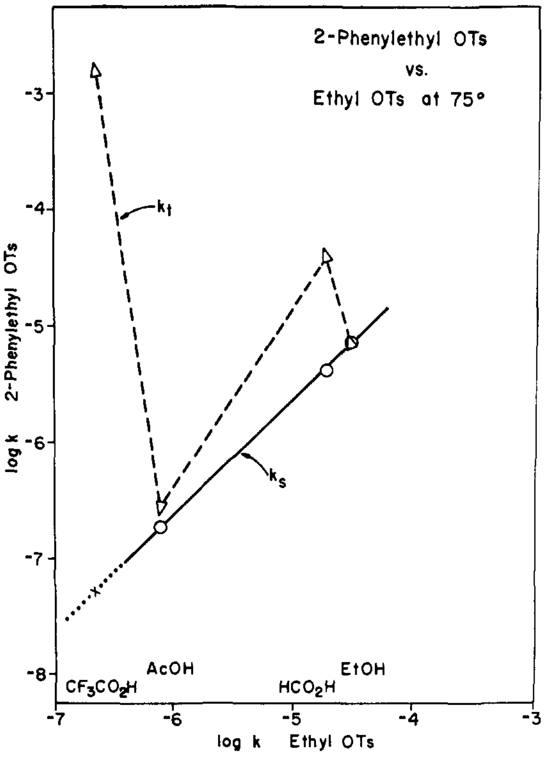

Figure 2.

threo-3-phenyl-2-butyl[3,10a,b,d] toluenesulfonate. The same general picture of competing k_Δ and k_s routes, with little or no leakage between them, and with (k_Δ/k_s) dependent on structure and solvent, applies generally to the simple primary and secondary β-arylalkyl systems.

Quite a different description of the solvolysis of the above systems has been evolved by Brown.[8] Without recognizing competing k_Δ and k_s processes in his discussion, his treatments of rates, phenyl substituent effects, solvent effects, and stereochemistry are unacceptable, in our opinion. Also, we believe that this failure to recognize relatively discrete k_Δ and k_s processes is the chief cause of his two great "anomalies in current carbonium ion theory."[8]

Lancelot and P. von R. Schleyer, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 9–13, 1968, Paper ORGN-40.

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The Stereochemistry of Decacoordination. The Molecular Structure of Bis(bipyridyl)lanthanum Nitrate

Sir:

As part of a program of study of the geometry of the coordination polyhedra in complex compounds of the lanthanides, we have determined the crystal and molecular structure of an adduct of lanthanum nitrate with 2,2′-bipyridyl, formulated as $La(NO_3)_3 \cdot 2bipy$. This particular molecule was chosen for study because the presence of a higher coordination number than eight was suspected if the capacity of the nitrate ions to act as bidentate ligands was utilized; and in addition, since only bidentate chelating ligands are involved, it was thought that information on the preferred ground-state geometry for decacoordination might be forthcoming from such an analysis. The only discrete molecular complex in which decacoordination has been rigorously established thus far is $La(H_2O)_4HA \cdot 3H_2O$, where H_4A is ethylenediaminetetraacetic acid.[1] Here, the geometry of the coordination polyhedron is determined primarily by the constraints of the chelating ligand.

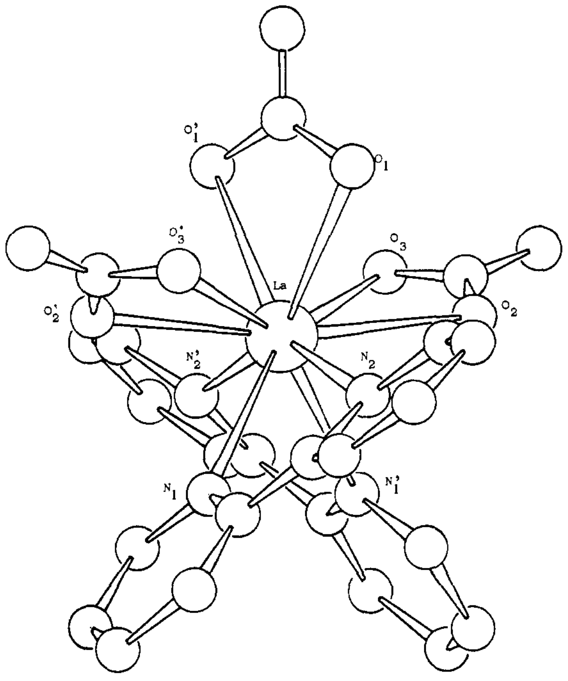

Figure 1. A perspective drawing of the $La(NO_3)_3 \cdot 2bipyridyl$ molecule, viewed down the x axis of the orthorhombic unit cell.

Crystals suitable for X-ray analysis were prepared as described by Hart and Laming[2] and were found to belong to the orthorhombic system, space group Pbcn, with four molecules in the unit cell. From intensity data collected on a General Electric manual diffractometer, utilizing Mo $K\alpha$ radiation in the moving crystal–moving counter technique, we have determined the molecular structure by the usual sequence of Patterson, Fourier, and least-squares calculations. The residual for 1514 reflections after two cycles of refinement, with anisotropic thermal parameters for the metal atom, and isotropic parameters for the light atoms, stands at 0.11 (0.078 for the nonzero data), and refinement is continuing.

From the illustration of the molecular structure given in Figure 1, it can be seen that the metal atom is in fact ten-coordinate, all three nitrate ligands being bidentate. The coordination polyhedron and the molecule are required to possess C_2 symmetry. The three metal–

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(1) M. D. Lind, B. Lee, and J. L. Hoard, *J. Amer. Chem. Soc.*, 87, 1611 (1965). A referee has drawn our attention to the fact that, during a recent symposium, Professor Hoard pointed out that the coordination polyhedron in this molecule approximates the bicapped square antiprism.

(2) F. A. Hart and F. P. Laming, *J. Inorg. Nucl. Chem.*, 27, 1825 (1965).

oxygen bond lengths are equal to within the estimated standard deviations, averaging 2.605 (0.011) Å, while the two metal–nitrogen bond distances are 2.665 (0.016) Å (N_1) and 2.648 (0.015) Å (N_2), respectively.

While the exact geometry of the coordination polyhedron in the molecule is to a certain extent controlled by the bite of the chelating ligands, we feel that it can be meaningfully described in terms of one of the possible models for the preferred ground-state geometry for decacoordination, *viz.*, the bicapped dodecahedron of D_2 symmetry.[3] In fact, reference to the eight-coordinate polyhedron is very useful since several features of this geometry are retained here. Thus, the oxygen and nitrogen atoms, O_3 and N_1, together with their symmetry-related pair and the lanthanum atom, are coplanar to within the esd's and correspond quite closely to one of the trapezoidal planes of the dodecahedron. The angular parameters θ_A and θ_B are 37.3 and 69.5°, respectively.[4] In addition, the nitrate ligand, bisected by the crystallographic twofold axis, spans the *a* edge of the second trapezoidal plane defined by La, O_1 and O_1', and N_2 and N_2'. However, these five atoms are far from coplanarity, N_2 and N_2' being *ca.* 1.10 Å from the plane defined by the metal atom, O_1, and O_1'. The dihedral angle between this latter plane and the first trapezoidal plane is 89.5° at the present level of refinement.

The arrangement of the four coordinating atoms O_2, O_2', N_2, and N_2' is primarily governed by the steric requirements of the nitrate groups and the rings of the bipyridyl molecules constituting the "equatorial" plane. However, if, as mentioned earlier, we consider the nitrogen atoms N_2 and N_2' as defining (together with O_1 and O_1') one of the trapezoidal planes of the dodecahedron, then the bipyridyl ligands span the g-type edges of this polyhedron while the ninth and tenth bonds, to the nitrate oxygen atoms, O_2 and O_2', pass approximately through the midpoints of the edges of type b, since the group of atoms La, N_2, O_2, and O_3 are almost coplanar. Allowing for the constraints of the chelating ligands, therefore, the approximation to an idealized bicapped dodecahedron is reasonably close.

The relevant nonbonded intramolecular distances defining the basic eight-coordinate polyhedron and also its extension to the ten-coordinate polyhedron are as follows: N_1N_1' (a) 3.23; N_1N_2 (g), 2.66; N_1N_2' (g), 3.81; N_1O_3' (m), 3.14; N_2O_3 (b), 4.60; N_2O_3' (b), 3.04; O_3O_1 (g), 2.96; O_3O_1' (g), 3.04; O_1N_2 (m) 3.49; O_1O_2, 2.87; N_2O_2 3.18; and N_1O_2, 3.05.

Investigation of a species with all ligands identical should throw further light on this coordination geometry, and to this end we are currently investigating the stereochemistry of the $Ce(NO_3)_5^{2-}$ complex ion.

Acknowledgment. We are grateful to the Iraqi Government for support of this research, in the form of a postgraduate fellowship to A. R. A.

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(3) E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), 21, 109 (1967). These authors list the maximum symmetry attainable as C_2.

(4) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 2, 235 (1963). See this paper for a definition of the nomenclature used here.

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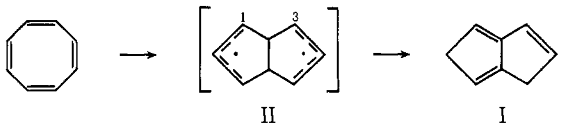
The Cyclooctatetraene–Dihydropentalene Rearrangement[1,2]

Sir:

It is becoming increasingly clear that a number of compounds of the empirical formula $(CH)_8$ share an energy surface quite as complex as that inhabited by the $(CH)_{10}$'s. Zimmerman[3a–c] has discovered the photochemical interconversions of barrelene, semibullvalene, and cyclooctatetraene. Recently Criegee and Askani[4] described the thermal conversion of octamethylcyclooctatetraene to octamethylsemibullvalene. We are prompted by this interest to report in preliminary form on the thermal rearrangement of cyclooctatetraene and to describe one new exit from the $(CH)_8$ energy surface.

Some years ago, Tanaka[5] investigated the gas- and liquid-phase pyrolysis of cyclooctatetraene. He found ethylene, acetylene, benzene, and styrene, and mentioned unidentified products. Like Tanaka we find benzene and styrene, but under some conditions the major product is the dihydropentalene I. Identification of this product was easy as it had been synthesized previously by Katz.[6] Although our route to I lacks the style of Katz' design, it is remarkably simple and rather large quantities of I can be obtained. Cyclooctatetraene was pyrolyzed in a flow system at 400–665° and the products were collected in a trap maintained at −78°. Figure 1 shows the product composition as a function of temperature. The residence time was kept at *ca.* 7.5 sec.



Two mechanistic extremes suggest themselves, each leading to the diradical II. This in turn suffers a series of 1,5 hydrogen shifts, ultimately arriving at I. One pathway leads through semibullvalene to II and draws on the report of Criegee[4] for analogy. Alternatively, II may be formed directly from cyclooctatetraene.[7] These are only extremes, of course, and merge into each other as the extent of bonding between carbons 1 and 3 in II increases.

A question unanswered by this work is whether other, degenerate rearrangements of lower activation energy are rendered invisible in the absence of a label. Indications that this may be so exist in the work of

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(1) This work was supported by a grant from the Research Corporation, to whom we express our appreciation. We are also grateful to the Badische Anilin und Soda-Fabrik for a generous gift of cyclooctatetraene.

(2) Taken from the B.A. Thesis of L. O. S., Princeton University, 1968.

(3) (a) H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967); (c) H. E. Zimmerman and H. Iwamura, *ibid.*, **90**, 4763 (1968).

(4) R. Criegee and R. Askani, *Angew. Chem.*, **80**, 531 (1968); *Angew. Chem. Intern. Ed. Engl.*, **7**, 537 (1968).

(5) I. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec.*, **75**, 212 (1954); *Chem. Abstr.*, 48, 4984*b* (1954).

(6) T. J. Katz, M. Rosenberger, and R. K. O'Hara, *J. Am. Chem. Soc.*, 86, 249 (1964).

(7) M. Stiles and U. Burckhardt, *ibid.*, 86, 3396 (1964). We thank Professor Stiles for discussions of unpublished work bearing on this point.