The stereochemical results[7] (Table II) indicate a high per cent retention which is approximately the same as that reported for the nitrosoamide decompositions of 1-phenylethylamine[5] and 3β-cholestanylamine[8] in acetic acid (OH and OD). Note that the solvent-derived products were formed with net retention of configuration (Table II).[9] The mechanism for the decomposition of III is presumably the same as that outlined for 1-phenylethylamine.[5]

(7) Using values of G. H. Green and J. Kenyon (*J. Chem. Soc.*, 751 (1950)) for benzhydrol, values of G. R. Clemo, C. Gardner, and R. Raper (*ibid.*, 1958 (1939)) for the amine, and the fact that all previous nitrosoamide reactions in polar solvents have proceeded with retention of configuration. Suitable controls were run to ensure the validity of the O-18 and stereochemical results.

(8) E. H. White and F. W. Bachelor, *Tetrahedron Letters*, 77 (1965).

(9) For a related example, see E. H. White and J. E. Stuber, *J. Am. Chem. Soc.*, 85, 2168 (1963), and for an example of retention observed in the solvolysis of a benzhydryl ester, see H. L. Goering, R. G. Briody, and J. F. Levy, *ibid.*, 85, 3059 (1963).

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Anomalous Rotatory Dispersion of 1-Butyl-1-*d* Acetate

Sir:

It is now established, both theoretically[1] and experimentally,[2] that molecules which are optically active because of hydrogen–deuterium asymmetry[3] do not differ in principle from normally asymmetric molecules.

Investigation of the optical rotatory dispersion (ORD) of several deuterium compounds, R_1CHDR_2, resulted in the observation of plain dispersion curves.[2] However, measurements could not be carried out in the region of electronic absorption due to the small optical activity and high absorptivity exhibited by these compounds. Since the Cotton effect is observed only in the vicinity of an absorption band, it was not possible to demonstrate experimentally whether molecules which are optically active because of H–D asymmetry are capable of exhibiting measurable Cotton effects.

We wish to report what we believe to be the first observation of a Cotton effect in a molecule which owes its optical activity solely to isotopic substitution.

(R)-(+)-1-Butyl-1-*d* acetate, (+)-1, $[\alpha]^{27}D$ +0.687°,

$$\begin{array}{c} D \\ | \\ CH_3CH_2CH_2\!-\!C\!-\!O_2CCH_3 \\ | \\ H \\ (+)\text{-}1 \end{array}$$
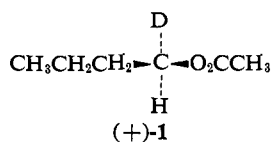
was prepared from (R)-(−)-butanol-1-d^4 by treatment

(1) W. Fickett, *J. Am. Chem. Soc.*, 74, 4204 (1952).

(2) A. Streitwieser, Jr., L. Verbit, and S. Andreades, *J. Org. Chem.*, 30, 2078 (1965); M. Sprecher, R. Berger, and D. B. Sprinson, *J. Biol. Chem.*, 239, 4268 (1964); J. W. Cornforth, G. Ryback, G. Popjak, C. Donninger, and G. Schroepfer, Jr., *Biochem. Biophys. Res. Commun.*, 9, 371 (1962). Professor H. S. Mosher, Stanford University, has very kindly communicated the results of some preliminary ORD measurements of derivatives of neopentyl alcohol-1-*d* made in 1960: H. S. Mosher and V. E. Althouse, unpublished work.

(3) A. Streitwieser, Jr., J. R. Wolfe, Jr., and W. D. Schaeffer, *Tetrahedron*, 6, 338 (1959).

(4) The 1-butanol-1-*d* was prepared via the asymmetric hydroboration reaction (A. Streitwieser, Jr., and L. Verbit, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, Abstracts, p 50N) and was 59% optically pure.[5] Nmr analysis indicated the presence of 0.97 ± 0.05 D per molecule.
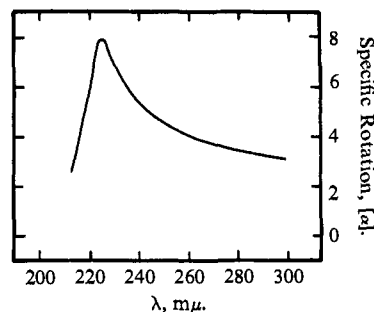
Figure 1. Optical rotatory dispersion curve of (R)-(+)-1-butyl-1-*d* acetate in isooctane solution.

with acetyl chloride and pyridine. Since preparation of the ester does not involve the asymmetric center, (+)-1 is also 59% of optical purity.

The ultraviolet ORD curve of (+)-1 in isooctane solution is shown in Figure 1. The first extremum of a positive Cotton effect is observed with a peak at 226 mμ. Because of a decreasing rotation:absorption ratio, measurements were possible only to 212 mμ.[6] The results of the ORD data for (+)-1 indicate that optically active deuterium compounds can be expected to exhibit weak but measurable Cotton effects.

(5) V. E. Althouse, D. M. Feigl, W. A. Sanderson, and H. S. Mosher, *ibid.*, 88, 3595 (1966), report $[\alpha]^{27.5}D$ 0.471° for 1-butanol-1-*d* prepared enzymatically.

(6) A JASCO recording spectropolarimeter was used. Measurements were carried out under constant nitrogen flush using the ±30 millidegree scale. In order to guard against instrument artifacts such as stray light, the sample absorbance was kept below 2. Base-line measurements were taken using unlabeled (thus inactive) *n*-butyl acetate in isooctane at the same concentration at which the optically active sample was run. A 450-w high-pressure xenon arc with less than 50 lamp-hr was used as the source.

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Fluorescence and Room-Temperature Laser Action of Trivalent Neodymium in an Organic Liquid Solution

Sir:

In two recent communications, we reported fluorescence and laser action of trivalent neodymium in an aprotic inorganic solvent.[1,2] The present communication extends this study to organic liquid systems.

Excited neodymium undergoes radiationless relaxation by two mechanisms: direct energy transfer to a vibration of the environment[3] and self-quenching.[4] Both the choice of the solvent and the design of the solute for the present system were aimed to reduce these.

(1) A. Heller, *Appl. Phys. Letters*, 9, 106 (1966).

(2) A. Lempicki and A. Heller, *ibid.*, 9, 108 (1966).

(3) A. Heller, *J. Am. Chem. Soc.*, 88, 2058 (1966).

(4) G. E. Peterson and P. M. Brindenbaugh, *J. Opt. Soc. Am.*, 54, 644 (1964).
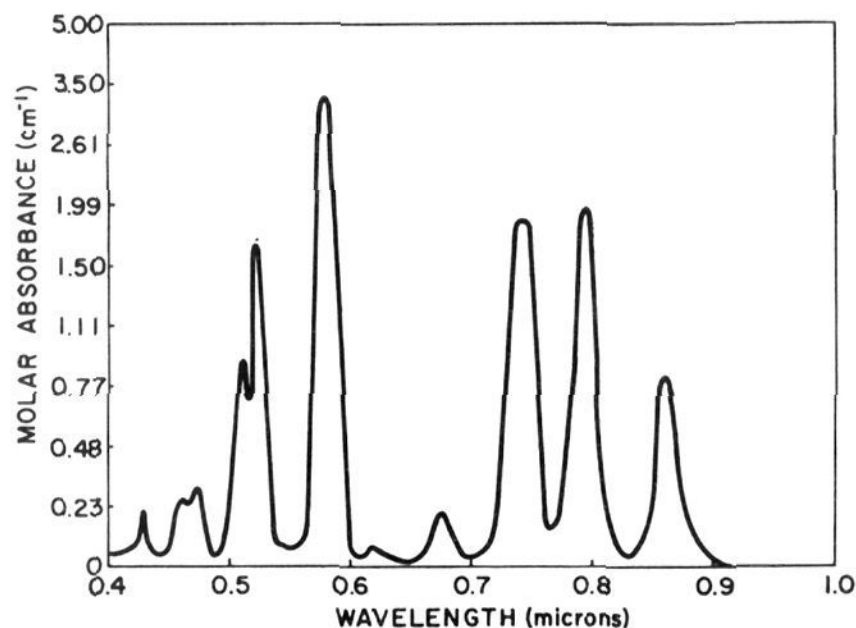
Figure 1. Absorption spectrum of the o-phenanthroline adduct of neodymium pentafluoropropionate in dimethyl sulfoxide-d_6.
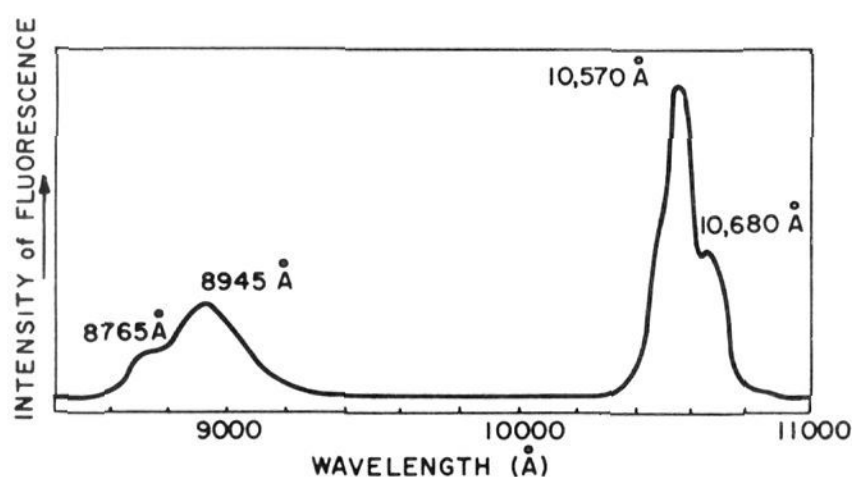

Figure 2. Spectrum of fluorescence of a 0.2 M solution of the o-phenanthroline adduct of neodymium pentafluoropropionate in dimethyl sulfoxide-d_6.
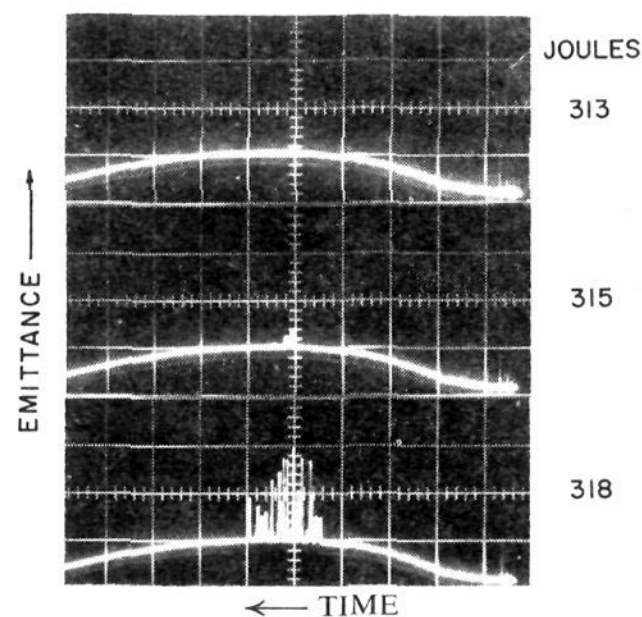

Figure 3. Laser action in a 0.2 M solution of the o-phenanthroline adduct of neodymium pentafluoropropionate in dimethyl sulfoxide-d_6. The horizontal time scale is 50 μsec/division. The vertical scale represents the relative emittance. The threshold for laser action is between 314 and 315 joules.

Our previous work on inorganic liquid solutions suggested that radiationless deexcitation of neodymium may be reduced by creating an environment in which high-energy vibrations are absent.[1] Early experiments in organic solutions indicated that the quenching interaction between the excited ion and vibrations of the neighboring molecules has a limited range: upon progressive removal of the sites of high-energy vibration from the vicinity of the rare earth, the quantum yield of luminescence increases rapidly. This is seen in the following progression. The quantum yield of an aqueous solution of neodymium chloride[5] is 10^{-4} times that of neodymium in a tin tetrachloride–selenium oxychloride solution. Replacement of the hydrogen of the water by deuterium increases the luminescence by a factor of 5. The replacement of water as the solvent by dimethylformamide, in which the solvating atom (oxygen) is not bound to a hydrogen atom, increases the luminescence by an order of magnitude. In dimethyl sulfoxide, where the hydrogens are removed yet another atom from the environment of the rare earth, the quantum yield is almost two orders of magnitude greater than that in aqueous solutions, and deuteration enhances the emittance by another factor of 3. (The yield in deuterated dimethyl sulfoxide is about two orders of magnitude less than that in selenium

oxychloride–tin tetrachloride, which contains no hydrogen or deuterium.[6]) Obviously, organic perhalocarbons could have been desirable solvents, since they have no atoms lighter than carbon. However, we could not find a neodymium-containing solute, free of high-energy vibrations, with sufficient solubility in perhalocarbons to yield solutions of reasonable emittance.

The active solutes were designed to meet four requirements: (a) solubility in dimethyl sulfoxide; (b) few high-energy vibrations (few hydrogen atoms); (c) maximum separation between the site of high-energy vibration and the rare earth ion (whenever the high-energy vibrations could not be completely excluded), thus eliminating compounds in which one of the coordinating atoms is bound to a hydrogen atom; (d) large anions, coordinating not more than one neodymium cation. This last requirement was posed in view of the self-quenching of neodymium[4] which is a short-range interaction (unless the neodymium concentration is extremely high and permits energy transfer by hopping).[7] The importance of ionic size and of coordination is indicated by our results on selenium oxychloride solutions of neodymium; in this solvent chloride solutions undergo self-quenching, while hexachloroantimonate or hexachlorostannate solutions do not.

One series of compounds which approximated our requirements were the o-phenanthroline adducts of the perhalo acid salts of neodymium. These are soluble in dimethyl sulfoxide, yielding dissolved complexes which apparently carry at least one molecule of dimethyl sulfoxide in their immediate solvation shells. The quantum yield of luminescence in these solutions is estimated to be $\sim 10^{-2}$; deuteration of the solvent brings the yield to $\sim 3 \times 10^{-2}$, which, although relatively low, is still sufficient for attainment of laser action.

The solution which we chose for our luminescence and laser studies was a 0.2 M dimethyl sulfoxide-d_6

(5) A. Heller, "Fifth Rare Earth Research Conference" Book 1, Institute for Atomic Research, Iowa State University, Ames, Iowa, 1965, pp 77–95.

(6) The emittance of the selenium oxychloride–tin tetrachloride solutions exceeds that of our continuous wave Nd–CaWO₄ single crystals, and we believe that the quantum yield of luminescence of these solutions may approach unity.

(7) A. D. Pearson and G. E. Peterson, Appl. Phys. Letters, 8, 210 (1966).

solution of the o-phenanthroline adduct of neodymium pentafluoropropionate. The adduct is prepared in two steps.[8] A solution of neodymium pentafluoropropionate in absolute alcohol is obtained by mixing stoichiometric amounts of a solution of neodymium chloride and a solution of sodium pentafluoropropionate, both saturated at room temperature, and filtering off the precipitated sodium chloride. On adding a solution of 1 equiv of o-phenanthroline in absolute alcohol, the alcoholate of the desired compound precipitates. Drying the solvate at 60° *in vacuo* removes the alcohol and yields the nonsolvated adduct. *Anal.* Calcd for $Nd(CF_3CF_2COO)_3 \cdot C_{12}H_8N_2$: Nd, 17.73. Found: Nd, 17.76. Solutions of the adduct in dimethyl sulfoxide have only a limited shelf life, presumably because of solvolysis of the adduct. For this reason, the spectra of absorption (Figure 1) and of emission (Figure 2) were run on freshly prepared solutions.

In the room-temperature laser experiment shown in Figure 3, we used a 5-cm long, 0.4-cm i.d. quartz cell, with flat and parallel windows having dielectric coatings of maximum reflectance at 1.06 μ^2. The cell was filled through a side arm in which sufficient space was left for the expansion of the liquid. The light, from the pumping source, two E.G.&G. FX-51 flashlamps in series, was filtered through 1 cm of 10% potassium dichromate in water. This filter is opaque to light below 4800 A and above 11,500 A.[9] The lamps were fed by an 80-μf capacitor through a 300-μ Hz choke. The light reaching an RCA 7102 photomultiplier detector was filtered by a 1.06-μ interference filter with a 0.02-μ band width.

As might be expected from the low quantum yield of luminescence, the thresholds of the present solutions were higher than those in the Nd^{3+}–$SeOCl_2$–$SnCl_4$ system. The limited shelf life and the photodecomposition of dimethyl sulfoxide by ultraviolet radiation[10] make the organic system a less desirable laser material than the previously reported inorganic liquid.[1] Nevertheless, the present liquid laser does have the advantage that the active liquid is not corrosive and, presumably, not toxic. Furthermore, in comparison with previously reported organic laser systems, involving chelates of europium, the power or the energy output in this system is not inherently limited by excessive absorbance of an organic ligand,[11] since the pump bands originate exclusively in the ion itself. The fact that the insertion of the ultraviolet-absorbing aqueous dichromate filter causes an improvement in the performance of the organic laser proves that, unlike in the former chelates, pumping does not take place through the organic ligand.

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(8) F. A. Hart and F. P. Laming, *J. Inorg. Nucl. Chem.*, 27, 1605 (1965).

(9) K. F. Tittel, *Rev. Sci. Instr.*, 35, 522 (1964).

(10) K. Mislow, M. Axelrod, D. R. Rayner, H. Gotthardt, L. M. Coyne, and G. S. Hammond, *J. Am. Chem. Soc.*, 87, 4958 (1965).

(11) A. Lempicki, H. Samelson, and C. Brecher, *Appl. Opt. Suppl.*, 2, 205 (1965).

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The Mechanism of the Formation of an Iridium Complex of Molecular Nitrogen *via* Organic Azides[1]

Sir:

Recent reports have described iridium[2] and ruthenium[3] complexes containing molecular nitrogen as a ligand. Aside from their novelty, interest in such complexes stems from the search for a catalyst to effect the hydrogenation of nitrogen under mild conditions. Stoichiometric fixation of nitrogen at atmospheric pressure through a presumably binuclear titanium complex has been partially elucidated.[4]

Herein are described the gross features of the mechanism (Figure 1) by which the iridium complex of nitrogen III is formed. The concepts inherent in this mechanism may be extended to the preparation of other nitrogen complexes and indeed to a wide range of π complexes.

Earlier it was reported[2] that Vaska's iridium complex I reacts with a series of acid azides to form the nitrogen complex III in high yield provided that the solvent $CHCl_3$ contained water or, as demonstrated herein, an alcohol. The following experimental observations lead us to propose the mechanism depicted in Figure 1.
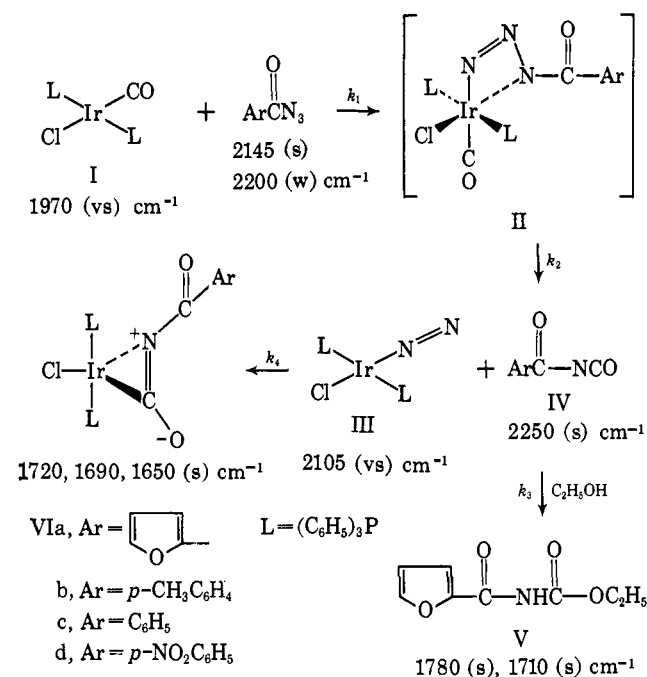

Figure 1.

When the reaction was carried out in reagent $CHCl_3$ (containing ethanol) using furoyl azide, the carbamic ester V was isolated from the reaction mixture as the major organic product and identified by complete elemental analyses, molecular weight, mass spectral pattern, and nmr and infrared spectra. Similarly, when the reaction was run in pure $CHCl_3$ to which other alcohols or water were added, the nitrogen com-

(1) This work was supported by the National Science Foundation and the Advanced Research Projects Agency Contract SD-100.

(2) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, 88, 3459 (1966).

(3) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).

(4) H. Brintzinger, *J. Am. Chem. Soc.*, 88, 4305 4307 (1966).