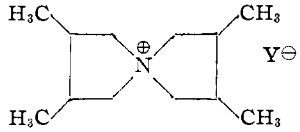
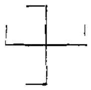
or both of these molecular symmetry elements is possessed by every inactive, non-racemic substance hitherto reported. However, it has long been recognized[2] that any molecule lacking a plane or center, but possessing a *fourfold alternating axis of symmetry*, would still be superposable on its mirror image; and it has been predicted[2] that any compound consisting of such molecules would be experimentally inactive and non-racemic.

We wish now to report the synthesis of what appears to be the first actual substance possessing this rare combination of symmetry elements, namely, the *meso* "*trans/trans*" diastereomer[3] of 3,4,3′,4′-tetramethylspiro-(1,1′)-bipyrrolidinium *p*-toluenesulfonate[4] (I).

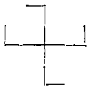


(I)

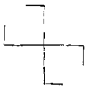
Four diastereomers (three active, one *meso*) would be predicted for this structure. All four have now been prepared. The configurations can be depicted conveniently by the "swastika" projection formulas[5] II–V. Only diastereomer V possesses the desired symmetry characteristics.



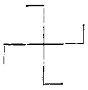
Active
cis/cis
II



Active
cis/trans
III



Active
trans/trans
IV



meso
trans/trans
V

meso-2,3-Dimethylbutane-1,4-diol[6a] was converted to its di-*p*-toluenesulfonate, m.p. 108–109.2°, Found: C, 56.06; H, 6.21; S, 14.56. The epimeric DL-diol gave a ditosylate melting at 107–108.3° (mixed m.p. with *meso* epimer depressed), Found: C, 56.43; H, 6.35; S, 14.71. The dextrorotatory diol (m.p. 44–45°, $[\alpha]^{21}D$ +5.38° (ether)) gave a levorotatory ditosylate, m.p. 90.5–91°, $[\alpha]^{21}D$ −7.67° (benzene); the levo-diol[7] gave a dextro ditosylate, 90.5–91.3°, $[\alpha]^{20}D$ +7.75°.

The preparation of *meso* and of DL-3,4-dimethylpyrrolidine has previously[6b] been described. The DL pyrrolidine treated with *dextro*-tartaric acid gave the crude "*dextro-dextro*" tartrate, m.p. 187–189°, $[\alpha]^{22}D$ +32.2° (water). Using *levo*-tartaric acid, the "*levo-levo*" tartrate was obtained and after twelve recrystallizations showed $[\alpha]^{25}D$ −36.2°, m.p. 187–189°, Found: N, 5.68. The liquid *dextro* pyrrolidine regenerated from the tartrate yielded a *p*-toluenesulfonate of m.p. 148–150.5°, $[\alpha]^{21}D$ +17.5° (water); the *levo* tosylate melted at 150–153°, $[\alpha]^{21}D$ −20.15°.

Reaction of *levo*-3,4-dimethylpyrrolidine with the above *levo*-ditosyldiol in hot dioxane finally gave the desired *meso trans/trans* bipyrrolidinium tosylate (I or V) which after recrystallization from tetrahydrofuran melted at 160–162°, optical rotation zero within experimental error[8]; Found: C, 63.93; H, 8.92; N, 4.09; S, 8.94. The identical product can be obtained by employing the dextrorotatory forms of both reactants.

However, reaction of the *dextro* pyrrolidine with *levo*-ditosyldiol gave a different and active *trans/trans* diastereomer IV, *p*-toluenesulfonate m.p. 150–152.5°, $[\alpha]^{30}D$ +19.88° (water). Since in this comparable reaction optical activity was not destroyed, it appears improbable that the observed inactivity of V is due merely to racemization.

Using appropriate intermediates, we have also prepared the DL-*cis/trans* diastereomer III, *p*-toluenesulfonate m.p. 181–182°, Found: C, 64.51; H, 8.97; N, 3.57, and its dextrorotatory form, m.p. 177.5–179°, $[\alpha]^{25}D$ +12.23° (water). Likewise we have made the DL/*cis/cis* diastereomer[9] II, *p*-toluenesulfonate m.p. 185.5–187°, Found: C, 64.27; H, 8.88; N, 3.57.

The limited evidence reported here is consistent with the prediction that a fourfold alternating axis of molecular symmetry would be a sufficient condition for optical inactivity.

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RECEIVED JULY 28, 1955

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[2] For an excellent discussion see G. W. Wheland, "Advanced Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, 1949, pp. 147–151. For earlier mention see Freudenberg, "Stereochemie," F. Deuticke, Leipzig, 1933, p. 601.

[3] The designation "*trans/trans*" signifies that both rings independently have *trans* configurations for the pairs of methyl groups.

[4] Strictly speaking it is the quaternary ammonium cation which has the symmetry elements described.

[5] To interpret the formulas, consider coaxis of the two rings to be perpendicular to paper. The intersecting lines represent the planes of the two rings. The short arms on each line show whether the substituents are *cis* or *trans*.

[6] G. E. McCasland and S. Proskow, (a) THIS JOURNAL, **76**, 3486 (1954); (b) *ibid.*, **76**, 6087 (1954).

[7] *levo*-2,3-Dimethylsuccinic acid was converted to its dextro dimethyl ester (*Ann.*, **538**, 1 (1939)), which on reduction gave the *levo*-diol, m.p. 44.5–45.5°, $[\alpha]^{25}D$ −5.42°. The *dextro*-diol was similarly prepared.

[8] Polarimetric observations with sodium D light at about 29° were made by three observers using two different solvents and concentrations.

[9] C. R. Noller and C. E. Pannell, THIS JOURNAL, **77**, 1862 (1955), have recently prepared the *cis/cis* diastereomer of the homologous bipiperidinium compound.

[10] On leave at Ohio State University, 1955–1956.

DIRECT ACTION OF COBALT GAMMA RADIATION ON NITRATE ION IN AQUEOUS SOLUTION

Sir:

In the decomposition of water by ionizing radiation, the 100 ev. yields of the intermediate H, OH, H_2 and H_2O_2 may be denoted by G_H, G_{OH}, G_{H_2} and $G_{H_2O_2}$, respectively. In the reduction of Ce^{++++} in 0.8*N* sulfuric acid by ionizing radiation, the 100 ev. yield of Ce^{+++} has been postulated[1] to be equal to $2G_{H_2O_2} + G_H - G_{OH}$ according to a mechanism in which H atom reduces Ce^{++++} and OH radical oxidizes Ce^{+++}.

Cobalt[60] gamma radiation induces[2] a reaction between Ce^{++++} and Tl^+ which increases the 100 ev. yield of Ce^{+++} from 2.52 to 7.85 in 0.8*N* sulfuric acid. The initial 100 ev. yield of Ce^{+++} is independent of the concentration of Tl^+ (10^{-5}

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[1] A. O. Allen, *Radiation Research*, **1**, 87 (1954).

[2] T. J. Sworski, forthcoming publication.

to 10^{-2} molar). It is proposed here that Tl^+ increases the rate of Ce^{++++} reduction through reaction with OH radical to form Tl^{++} which reduces Ce^{++++} according to the following sequence of reactions.

$$Tl^+ + OH \longrightarrow Tl^{++} + OH^- \qquad (1)$$

$$Tl^{++} + Ce^{++++} \longrightarrow Tl^{+++} + Ce^{+++} \qquad (2)$$

According to this mechanism, the 100 ev. yield of Ce^{+++} increased by Tl^+ should be equal to $2G_{H_2O_2} + G_H + G_{OH}$. The previously reported[3] values for $G_{H_2O_2}$, G_H and G_{OH} of 0.78, 3.70 and 2.92, respectively, would predict a value for $2G_{H_2O_2} + G_H + G_{OH}$ of 8.18. The difference between 8.18 and 7.85 is real and may indicate the importance of reaction 3

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \qquad (3)$$

in regions of high ionization density as reported by Hart.[4]

NO_3^- also increases the rate of Ce^{++++} reduction in 0.8*N* sulfuric acid. It has been proposed[5] that in nitric acid solutions the reduction of Ce^{++++} is increased through reaction of OH radical with NO_3^-. Figure 1 shows that, in 0.8*N* sulfuric acid, NO_3^- increases the 100 ev. yield of Ce^{+++} when Tl^+ is present by the same amount as when Tl^+ is absent. This is interpreted as conclusive experimental evidence that the increase in 100 ev. yield of Ce^{+++} by NO_3^- is not attributable to OH radical reactions since the OH radicals are being efficiently utilized by Tl^+. If NO_3^- reacts with the H and OH radicals in a manner similar to that reported[6] for NO_2^-, the products must react with Ce^{++++} and Tl^+ in a manner equivalent to H and OH.

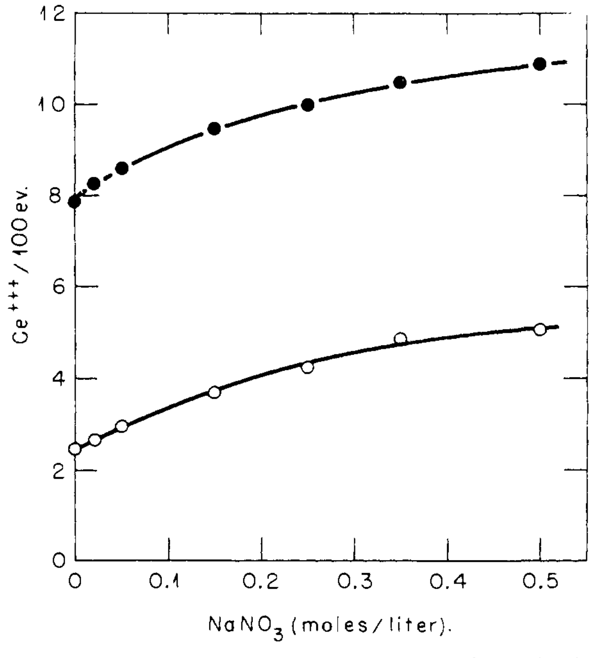

Fig. 1.—Effect of $NaNO_3$ on the reduction of ceric ion in 0.8 *N* sulfuric acid solutions; Ce^{++++} concentration in all solutions was initially 4×10^{-4} molar: ○, Tl^+ absent; ●, 2×10^{-3} molar Tl^+.

An alternative mechanism for the effect of NO_3^- is the direct action of gamma radiation on NO_3^-. This direct action is considered as resulting from excitation of the NO_3^- with resultant decomposition to NO_2^- as in the photochemical reduction[7] of NO_3^-. Ce^{++++} is then reduced by NO_2^-. NO_3^- excitation may result from the action of subexcitation electrons[8,9] or from the direct transfer of excitation energy from the excited water molecules (before collisional deactivation) to NO_3^-.

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[3] T. J. Sworski, THIS JOURNAL, **76**, 4687 (1954).

[4] E. J. Hart, *Radiation Research*, **2**, 33 (1955).

[5] G. E. Challenger and B. J. Masters, THIS JOURNAL, **77**, 1063 (1955).

[6] H. A. Schwarz and A. O. Allen, *ibid.*, **77**, 1324 (1955).

[7] E. Warburg, *Sitzb. Preuss. Akad. Math.-Phys. Kl.*, 1228 (1918); *Chem. Abs.*, **14**, 1930 (1920).

[8] J. Weiss, *Nature*, **174**, 78 (1954).

[9] R. L. Platzman, *Radiation Research*, **1**, 558 (1954); **2**, 1 (1955).

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RECEIVED AUGUST 8, 1955

THE USE OF PERFLUOROCARBOXYLIC ACIDS AS SEPARATING AGENTS[1]

Sir:

We have found that the perfluorocarboxylic acids[2] are useful extracting and separating agents for a wide variety of cations in aqueous solution. Using ethyl ether as the second solvent the extraction is found to depend on (a) the *p*H of the aqueous layer; (b) the ionic charge on the cation; (c) the nature of the anions present. Using perfluorobutyric acid as the extracting agent, trivalent cations, *e.g.*, Fe(III), Al(III), Cr(III), and a few divalent cations, UO_2(II), Be(II) can be effectively separated from monovalent and other divalent cations. With perfluoroöctanoic acid as the extracting agent, divalent cations, *e.g.*, Ca(II), Mg(II), Fe(II), Pb(II), Zn(II), etc., can be separated from monovalent cations.

It is generally found that the extraction proceeds best at a *p*H just less than that at which the cation would form an insoluble hydroxide. In line with this observation it is found that the extracted species is a basic salt.[3] Analyses of crystalline products obtained on evaporating the ether extracts indicate formulas such as $Fe(OH)(C_3F_7COO)_2 \cdot 2H_2O$; $Al(OH)(C_3F_7COO)_2 \cdot 2H_2O$; $Be(OH)(C_3F_7COO) \cdot 5H_2O$.

The separation factors for individual extractable species vary from 4–400 when the metal is dissolved in aqueous solution as the nitrate or perchlorate. Other anions will interfere with the extraction in some degree; fluoride and sulfate in particular are found to prevent extraction under conditions employed so far in this work. In the absence of interfering anions no salting agent is necessary although the separation factor obtained is, of course, influenced by the relative proportion of the perfluoroacid to the metallic ion.

While monovalent cations are not extracted,

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[1] This work was done at the Oak Ridge Gaseous Diffusion Plant operated for the Government by Union Carbide and Carbon Corporation.

[2] These acids may be obtained from the Minnesota Mining and Manufacturing Company, Minneapolis, Minnesota. We wish to thank them for samples supplied us in the early stages of this work.

[3] The calcium (II) ion appears to extract as a normal salt and is an exception to this generalization.