with the two asymmetric nitrogen centers should be interconvertible, as observed for I[2,3]); and (iii) isomerism associated with the position of the methyl groups of the diaminopropane residues, which could be *cis* or *trans* with respect to the nickel ion and/or adjacent to amino or imino groups.

A full X-ray structural investigation of the "yellow" isomer[1] as the perchlorate[4] has revealed the molecular structure II, with *trans* (1,8) imino groups, with both the asymmetric carbon and nitrogen centers racemic, with the adjacent C–H and N–H of the asymmetric centers on opposite sides of the molecular plane, and with the methyl groups of the diaminopropane residues in "axial" (2,9) positions adjacent to the imino groups.

The space group of the "orange" isomer[1] perchlorate, requires the nickel ion to be on a center of symmetry; *i.e.*, both the asymmetric carbon and nitrogen centers must be *meso*, the imino groups *trans* (7,14), and the diaminopropane residue methyl groups *trans* in 2,9 or 3,10 positions. Since the two isomeric products are formed in approximately equal amounts when tris(diaminopropane)nickel(II) reacts with acetone, it is reasonable to conclude that they are the C-*rac* and C-*meso* isomers of II. Two configurations are possible, with the hydrogen atoms of the adjacent asymmetric carbon and nitrogen centers on the same, or opposite, sides of the "molecular plane."

Confirmation of these structural assignments is provided by pmr spectra. The pmr spectra of the "orange" and "yellow" isomers (Table I) closely resemble those of the N-*meso* and N-*rac* isomers of I,[3] with in each case an additional doublet assigned to equivalent diaminopropane residue methyl groups. For the "yellow" C-*rac* isomer this methyl group is in an axial site, insofar as this terminology is appropriate to the imine end of the diaminoethane chelate ring. Deshielding by the nickel(II)[3] ion is less than for the axial geminal methyl group, and is obviously dependent on details of conformation. The similar σ value observed for the "orange" C-*meso* isomer supports assignment of these methyl groups to axial sites for this compound also.

Table I. Pmr Spectra, Methyl Group Resonances[a]

	A[b]	*B*[c]	*C*[d]	*D*[e]
"Orange" isomer[f]	1.22	1.29, 1.40	2.68	2.25
N-*meso*-I[g]	1.25	...	2.71	2.19
"Yellow" isomer[f]	1.18	1.48, 1.59	2.13	2.20
N-*rac*-I[g]	1.25	...	2.02	2.17

[a] Measured in acidified D_2O using a Varian HR60 spectrometer and with NaTPS as internal standard, σ values in ppm. [b] Equatorial component of *gem*-dimethyl group. [c] Diaminopropane residue methyl group. [d] Axial component of *gem*-dimethyl group. [e] Imine methyl group. [f] As tetrachlorozincate. [g] As thiocyanate. Values from ref 3 relative to an external TMS standard have been adjusted (−0.5 ppm) for convenience in comparison.

Reaction of tris[(+)-1,2-diaminopropane)]nickel(II) perchlorate or tris[(−)-1,2-diaminopropane)]nickel(II) perchlorate with acetone yields the enantiomorphs of the "yellow" racemate (product from (+)-1,2-diaminopropane, α_D +151°; product from (−)-1,2-diaminopropane, α_D −150.6°)

The monohydroperchlorate of (±)-1,2-diaminopropane reacts with acetone, diacetone alcohol, or mesityl oxide to form crystalline III·$2HClO_4$[5] analogous to the compound formed with diaminoethane.[6] This product reacts with nickel(II) to form C-*meso*-II, and therefore III is assigned the C-*meso* configuration. Failure to isolate any C-*rac* isomer apparently results from a higher solubility of the C-*rac* salt, (−)-1,2-diaminopropane hydroperchlorate yielding no crystalline product under these conditions. The formation of C-*meso*-II from III·$2HClO_4$ confirms the tetraazacyclotetrodecadiene structure for III, rather than the possible dihydrodiazapene IV, which would be expected to form a mixture of C-*meso*- and C-*rac*-II.[7]

Reaction of bis(diaminopropane)copper(II) perchlorate with acetone at 110° is reported[8] to form a macrocyclic copper(II) complex analogous to II, in low yield. At room temperature tris(diaminopropane)copper(II) perchlorate reacts slowly with acetone to form this compound and an isomeric product. The previously reported compound is also formed from III·2-$HClO_4$ and is therefore assigned the C-*meso* configuration. The new compound crystallizes with cell dimensions similar to C-*rac*-II·$2ClO_4$, supporting assignment as the C-*rac* isomer.

Crystal Data. C-*rac*-(2,4,4,7,9,11,11,14-Octamethyl-1,5,8,12-tetraazacyclotetradeca-1,8-diene)nickel(II) perchlorate[9] ("yellow" isomer): monoclinic, $P2_1/c$, a = 16.55, b = 10.90, c = 15.10 Å; β = 90° 55′; for Z = 4, D_c = 1.42; D_m = 1.45 g cm^{-3}.

C-*meso*-(2,4,4,7,9,11,11,14-Octamethyl-1,5,8,12-tetraazacyclotetradeca-1,8-diene)nickel(II) perchlorate ("orange" isomer): monoclinic, $P2_1/c$; a = 10.13, b = 8.37, c = 14.38 Å; β = 100° 5′; for Z = 2, D_c = 1.56; D_m = 1.52 g cm^{-3}.

C-*rac*-(2,4,4,7,9,11,11,14-Octamethyl-1,5,8,12,tetraazacyclotetradeca-1,8-diene)copper(II) perchlorate: orthorhombic, Pbcm or $Pbc2_1$; a = 15.80, b = 15.28, c = 10.41 Å; for Z = 4, D_c = 1.47; D_m = 1.50 g cm^{-3}.

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(3) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, **89**, 703 (1967); **90**, 6938 (1968).

(4) Approximately 2600 independent reflections; current *R* index of 0.15.

(5) *Anal.* Calcd for $C_{18}H_{36}Cl_2N_4O_8$: C, 42.7; H, 7.2. Found: C, 42.3; H, 7.4.

(6) N. F. Curtis and R. W. Hay, *Chem. Commun.*, 524 (1966).

(7) Further support has been presented elsewhere: N. F. Curtis, *Coord. Chem. Rev.*, **3**, 21 (1968).

(8) M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 3016 (1962).

(9) Since the original preparation,[1] a hydrate has nucleated, and the anhydrous salt no longer crystallizes. Failure to notice this change resulted in some incorrect deductions about the structures of these compounds (ref 7, p 10).

N. F. Curtis
Chemistry Department, Victoria University
Wellington, New Zealand

D. A. Swann and T. N. Waters
Chemistry Department, University of Auckland
Auckland, New Zealand

I. E. Maxwell
Chemistry Division, Scientific & Industrial Research Department
Wellington, New Zealand

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Measurement of Optical Activity in Racemic Mixtures

Sir:

Chiral molecules absorb left and right circularly polarized light to a different extent. A measure for this effect is the dissymmetry factor g.

$$g = \frac{\epsilon_L - \epsilon_R}{{}^1\!/_2(\epsilon_L + \epsilon_R)} = \frac{\Delta\epsilon}{\epsilon}$$

ϵ is the mean decadic molecular extinction coefficient. As theoretically expected and experimentally confirmed, circular dichroism has its counterpart in emission (circular polarization of luminescence; CPL).[1] Again a dissymmetry factor can be defined

$$g_{\text{lum}} = \frac{I_L - I_R}{{}^1\!/_2(I_L + I_R)} = \frac{\Delta I}{I}$$

I_L (I_R) is the quantity of emitted left (right) circularly polarized light in relative quanta per frequency interval.

Measurement of CD requires one of the two optical isomers in the pure state, whereas measurement of CPL offers a possibility to escape from this restriction. Upon irradiation of a racemic mixture with, for instance, left circularly polarized light one optical isomer will be preferentially excited (with a factor $(1 + g/2)/(1 - g/2)$ as compared to the other isomer). Consequently the luminescence will exhibit a dissymmetry factor

$$g_L = \frac{I_L{}^L - I_R{}^L}{{}^1\!/_2(I_L{}^L + I_R{}^L)} = {}^1\!/_2 g(\lambda_1) g_{\text{lum}}(\lambda_2)$$

(since g and g_{lum} vary with wavelength, g_L will depend upon the wavelength of excitation (λ_1) and observation (λ_2)).

If the excitation light is right circularly polarized we find

$$g_R = \frac{I_L{}^R - I_R{}^R}{{}^1\!/_2(I_L{}^R + I_R{}^R)} = -\,{}^1\!/_2\, g(\lambda_1) g_{\text{lum}}(\lambda_2)$$

Monochromatic circularly polarized light was obtained from a 450-W Xenon lamp, Cary double-prism monochromator, and circular polarizer (calcite Glan prism; quartz quarterwave plate). The luminescence was observed perpendicularly to the excitation beam. By means of a circular analyzer, consisting of a rotating quartz retardation plate followed by a polaroid polarizer, phase-sensitive detection methods could be used to determine $I_L - I_R$. Simultaneously ${}^1\!/_2(I_L + I_R)$ was recorded. The measuring equipment was calibrated by placing solutions of well-known optically active compounds between a luminescing nonoptically active compound and the circular analyzer and measuring their CD. It appeared that $(I_L - I_R)/[{}^1\!/_2(I_L + I_R)]$ could be determined within 1×10^{-3}. A solution of racemic *trans*-β-hydrindanone in isooctane (10^{-2} *M*) irradiated with 317-nm light yielded $gg_{\text{lum}} = +4 \times 10^{-3}$ (separate measurement of g at 317 nm, and g_{lum} as an average over the whole emission band yielded values of $+0.17$ and $+19 \times 10^{-3}$, respectively, for the + isomer, so that their product gg_{lum} equals $+3.2 \times 10^{-3}$).[2]

If one would know beforehand that g is equal to g_{lum}, this method would allow a direct determination of the rotational strength of an absorption band of an optically active molecule without actually isolating it from a racemic mixture. In many cases g will be different from g_{lum} which complicates the theoretical interpretation. Irrespective of this limitation one can obtain the form of the g curve by exciting at several wavelengths (as one can find the form of the g_{lum} curve upon irradiation at a fixed wavelength). The method may also be of practical value in ascertaining whether a compound that does not show ORD or CD is a racemic mixture or a *meso* structure. Another possible application is the study of chiral conformations of systems whose lifetimes are on the one hand long enough to prevent racemization in the excited state but on the other hand too short to permit resolution in the ground state.

Finally, transfer of excitation energy between one optical isomer and the other or excimer formation between them will decrease the effect of the preferential excitation. These effects may therefore be detected by this technique because the observed g_L will be lower than the value calculated with the above-mentioned equation.

H. P. J. M. Dekkers, C. A. Emeis, L. J. Oosterhoff
State University, Leiden
The Netherlands

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[1] C. A. Emeis, Ph.D. Thesis, University of Leiden, 1968; C. A. Emeis and L. J. Oosterhoff, *Chem. Phys. Letters*, 1, 129 (1967).

[2] The observed luminescence may be the fluorescence of an excimer,[3] in which case the above-mentioned expressions for g_L and g_R need not apply. No deviation from them could be detected with the presently available instrument.

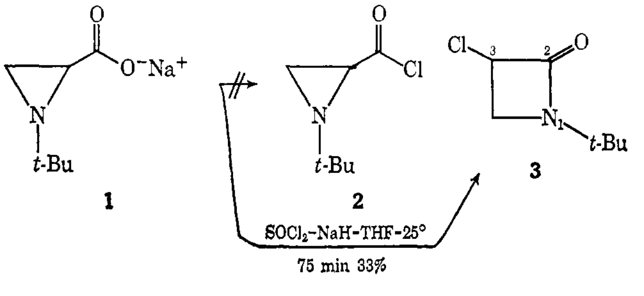
[3] M. O'Sullivan and A. C. Testa, *J. Am. Chem. Soc.*, 90, 6246 (1968).

A New Route to β-Lactams

Sir:

Elucidation of the penicillin and cephalosporin structures has stimulated a continuing interest in the development of new synthetic routes to biologically active β-lactams.[1] We wish to report that entry into functionally substituted β-lactams can be achieved by ring expansion of the aziridine ring.

Reaction of **1** with $SOCl_2$ yielded a neutral compound ($C_7H_{12}NOCl$)[2] instead of the usual acid chloride (**2**). We have assigned the 1-*t*-butyl-3-chloro-2-azetidinone structure (**3**) to this compound on the basis of its physical and spectral [*e.g.*, ir (liquid film) 1760 cm^{-1} (C=O)] properties. Additional confirmation for the β-lactam structure was obtained from the Zn–EtOH reduction[3] of **3** to 1-*t*-butyl-2-azetidinone.[4]



Some initial observations concerning the scope of this reaction are also relevent to defining the reaction mechanism. For example, the conversion of **1** to **3** could also be affected by oxalyl chloride in benzene with (29%) or without (26%) added Et_3N. The sim-

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[1] A. K. Bose, G. Spiegelman, and M. S. Manhas, *J. Am. Chem. Soc.*, 90, 4506 (1968); E. J. Corey and A. M. Felix, *ibid.*, 87, 2518 (1965).

[2] Satisfactory elemental and spectral (nmr, ir, and mass) analyses were obtained for all compounds unless otherwise indicated.

[3] *Cf.* I. L. Knunyants and N. P. Gambaryan, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 834 (1957); *Bull. Akad. Sci. USSR, Div. Chem. Sci.*, 855 (1957).

[4] This material was shown identical with that prepared (7% yield) from the reaction of *t*-butylaminopropionic acid with $SOCl_2$ and Et_3N.