Circular Dichroism of the Nitrogen Chromophore in the Open-chain Secondary Amine (*R*)-3,3-Dimethyl-2-methylaminobutane

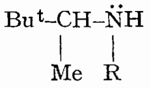
By Piero Salvadori*, Carlo Bertucci, Carlo Rosini, and Raffaello Lazzaroni

(*Centro di Studio del C.N.R. per le Macromolecole Stereoordinate ed Otticamente Attive, Istituto di Chimica Organica, Facoltà di Scienze M.F.N., Università di Pisa, Italy*)

Summary C.d. and u.v. absorption bands of (*R*)-3,3-dimethyl-2-methylaminobutane in the 250—180 nm spectral region are reported and assigned to Rydberg-type transitions on the basis of c.d. data at low temperature.

The c.d. spectrum of a simple nitrogen chromophore for wavelengths down to 180 nm has not been reported for an open-chain amine and the assignment of the related electronic transitions is still uncertain.[1] In order to obtain clear experimental evidence for a definitive assignment of the long-wavelength absorption bands[2] u.v. and c.d. spectra (from 250 to 180 nm) of the (*R*)-3,3-dimethyl-2-methylaminobutane (I) have been recorded under different conditions of phase, solvent, and temperature.

Compound (I) was obtained[3] by converting the primary amine (*R*)-3,3-dimethyl-2-aminobutane (II) into the corresponding ethyl carbamate (III) by reaction with ethyl chloroformate. Reduction of (III) with $LiAlH_4$ in tetrahydrofuran gave a good yield (*ca.* 90%) of the secondary amine (I), b.p. 114 °C, d_4^{25} 0·7553, n_D^{25} 1·4106, $[\alpha]_D^{25}$ −56·47° (neat). The enantiomeric purity (92%) of (I) was evaluated by n.m.r. spectroscopy and g.l.c., by determining the relative amounts of the diastereoisomeric amides obtained by reaction of (I) with (*R*)-α-methoxy-α-trifluoromethylphenylacetyl chloride.



$$\mathrm{Bu^t{-}\underset{\displaystyle Me}{\underset{|}{C}H}{-}\underset{\displaystyle R}{\underset{|}{\ddot{N}}H}}$$

(I) R = Me
(II) R = H
(III) R = CO_2Et

The u.v. spectrum in the vapour phase between 250 and 185 nm (Figure 1) shows a band centred at 195 nm (ϵ_{max} 2000). The maximum is blue shifted to 187 nm (ϵ_{max} 2400) in n-heptane. A larger blue shift is observed in a protic solvent like methanol (Figure 1) and the acid solution is completely transparent down to 190 nm.

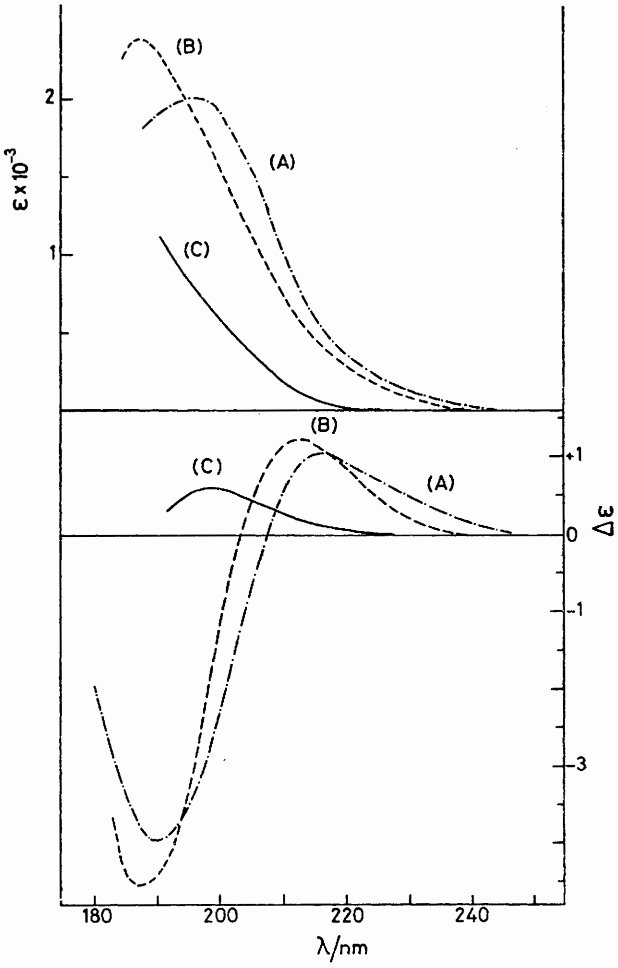


Figure 1. U.v. (upper curves) and c.d. (lower curves) spectra of (I): (A), vapour phase; (B), n-heptane; (C), methanol, at room temperature.

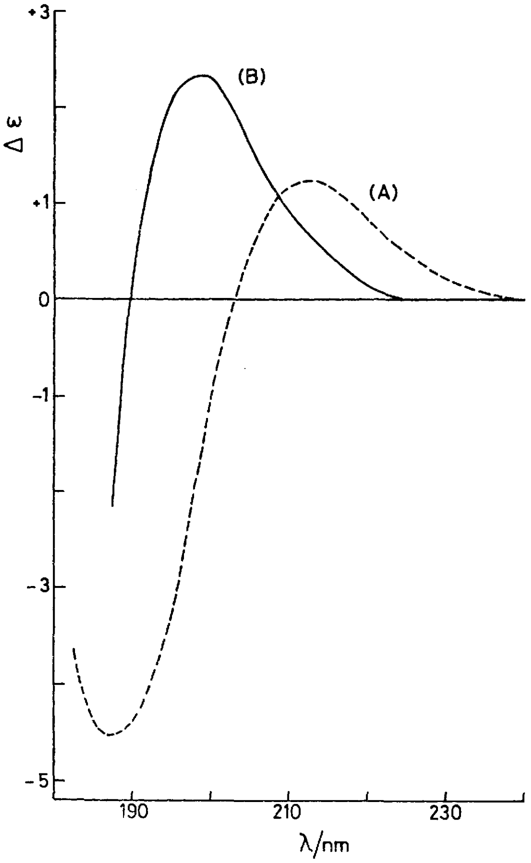


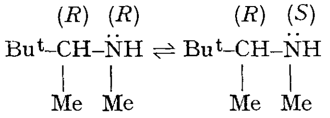
FIGURE 2. C.d. spectra of (I): (A), in n-heptane at room temperature; (B), in methylcyclohexane–isopentane (1:3) at −175 °C.

The c.d. spectrum in the vapour phase (Figure 1) shows a positive band at 216 nm ($\Delta\epsilon_{max}$ + 1) and a negative band at 189 nm ($\Delta\epsilon_{max}$ −4). The behaviour of the c.d. bands strictly follows that of the u.v. absorptions in going from the gas phase to solutions in n-heptane, methanol, and in acid solution. A blue shift of both the bands is observable in n-heptane (λ_{max} 213 nm, $\Delta\epsilon_{max}$ + 1·2; λ_{max} 187 nm, $\Delta\epsilon_{max}$ −4·5), only a positive band (λ_{max} 200 nm, $\Delta\epsilon_{max}$ + 0·6) appears in methanol, and the dichroic absorptions are completely absent (down to 190 nm) in acid solution. These results, in agreement with u.v. spectral data of simple aliphatic amines,[4] indicate that non-bonding electrons of the nitrogen atom are involved in the two transitions.

Additional information was obtained from the change of c.d. spectrum of (I) with temperature (Figure 2). A remarkable blue shift of both the bands is observed going from +20 to −175 °C, in hydrocarbon solution; at the same time, the intensity of the lowest-energy band is doubled ($\Delta\epsilon_{max}$ + 1·2 at +20 °C, $\Delta\epsilon_{max}$ + 2·4 at −175 °C).

While the lowest-energy band has been assigned[5] to a Rydberg transition ($n \rightarrow 3s$), there is uncertainty over the highest-energy band, which has been assigned either to an $n \rightarrow \sigma^*$ transition,[6] or to a Rydberg $n \rightarrow 3p$ transition.[5] Our results are in keeping with the latter assignment because a marked blue shift of both dichroic absorptions takes place with decreasing temperature (Figure 2), as expected for Rydberg-type transitions.[7]

The remarkable increase of the low-energy dichroic absorption with decreasing temperature is observable not only for (I), as already shown, but also for the corresponding primary amine (λ_{max} 215 nm, $\Delta\epsilon_{max}$ + 0·13 at 20 °C; λ_{max} 199 nm, $\Delta\epsilon_{max}$ + 0·96 at −175 °C, in hydrocarbon solution). A higher conformational homogeneity at low temperatures could explain the c.d. increase for both (I) and (II). However, in (I), asymmetric induction of the vicinal carbon atom on the chiral nitrogen atom can, in principle, take place. However, it is worth noting that the differences in c. d. intensity observed in the two cases could also arise because of the occurrence, for (I), of the epimerisation reaction (1), with an equilibrium constant different from unity.



$$\underset{\text{Me}}{\overset{(R)}{\text{Bu}^t\text{–CH}}}\text{–}\underset{\text{Me}}{\overset{(R)}{\ddot{\text{N}}\text{H}}} \rightleftharpoons \underset{\text{Me}}{\overset{(R)}{\text{Bu}^t\text{–CH}}}\text{–}\underset{\text{Me}}{\overset{(S)}{\ddot{\text{N}}\text{H}}} \qquad (1)$$

(*Received*, 9*th June* 1977; *Com.* 562).

---

[1] G. Gottarelli, B. Samori, G. L. Bendazzoli, P. Palmieri, and A. F. Drake, *Chem. Phys. Letters*, 1977, **45**, 318.

[2] J. H. R. Parello and F. Picot, *Tetrahedron Letters*, 1968, 5083; G. Kostianovsky, I. M. Gella, V. I. Markov, and Z. E. Samojlova, *Tetrahedron*, 1974, **30**, 39; W. Klyne, P. M. Scopes, R. N. Thomas, J. Skolik, J. Gawrosnky, and M. Wiewiorowsky, *J.C.S. Perkin I*, 1974, 2565.

[3] P. L. Mannella, R. Lazzaroni, and P. Salvadori, *Chimica e Industria*, 1975, **57**, 494.

[4] E. Tannenbaum, E. M. Coffin, and A. J. Harrison, *J. Chem. Phys.*, 1953, **21**, 311.

[5] M. B. Robin, 'Higher Excited States of Polyatomic Molecules,' Academic Press, London, 1974, p. 208.

[6] L. W. Pickett, M. E. Corning, G. M. Wieder, D. A. Semenow, and J. M. Buckley, *J. Amer. Chem. Soc.*, 1953, **75**, 1618.

[7] A. F. Drake, *J.C.S. Chem. Comm.*, 1976, 515.