sesquinorbornene, respectively. The electron density distribution within the double bond is clearly elongated along the π direction. The density distributions of single bonds C1–C2 and C11–C12 have rotational symmetry.

All the bonding maxima of the spiro three-membered ring (C7, C8, C9) are shifted by large amounts (0.27 Å average) outward from the bond axes, as one has come to expect for the bent bond of a cyclopropane ring system. The lines from the atoms to the corresponding bonding maxima (M) make angles M–C–M of 87.8° on the average. The corresponding C–C–C bond angles are 60.0°. An angle of 78.8° had previously been calculated between the bond paths of cyclopropane itself.[10] The central region of the three-membered ring has a flat plateau of 0.1 e $Å^{-3}$. Similar results have been found in other cyclopropane derivatives.[11]

An air-stable *syn*-sesquinorbornatriene recently synthesized[1,12] was shown to possess a central double bond having still greater downward pyramidalization (22.7°).

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft (H.I.) and the National Institutes of Health (L.P.) for their financial support of this work.

Registry No. 1, 85222-09-9.

Supplementary Material Available: Tables of bond distances, bond angles, positional parameters, and anisotropic thermal parameters for **1** (3 pages); tables of observed and calculated structure factors for **1** (68 pages). Ordering information is given on any current masthead page.

---

[10] Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985.

[11] Nijveldt, D.; Vos, A. *Acta Crystallogr.* **1988**, *B44*, 289.

[12] Paquette, L. A.; Shen, C.-C.; Krause, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2351.

Detection of Singlet–Triplet Transitions in Circular Dichroism. A Study of 2-Aminobutane

Anat Basil and Aharon Gedanken*

Department of Chemistry, Bar-Ilan University
Ramat Gan 52100, Israel

Received July 17, 1989

Singlet–triplet transitions (STT) are forbidden in optical absorption and can be detected only by using long optical cuvettes or a multiple reflection cell.[1] These transitions were unambiguously identified by electron-impact spectroscopy[2] and other techniques and are characterized by a small molar absorption coefficient ranging between 1 and 10^{-4}. For optically active molecules, STT can be detected by using circular polarized luminescence.[3]

This last emission detection method would a priori suggest that STT should be amenable also to circular dichroism (CD) absorption detection techniques. This is because the intensity of a circular dichroism signal is determined by the rotatory strength R, which is given by eq 1,

$$R = Im\{\langle g|\mu|e\rangle\langle e|m|g\rangle\} \qquad (1)$$

where g and e are the ground and excited electronic states, respectively, and μ and m are the electric and magnetic dipole operators. The magnetic dipole operator is defined by[4] eq 2,

$$m = (e/2mc)\sum_i\{\mathrm{Li} + 2\mathrm{Si}\} \qquad (2)$$

where Li is the orbital angular momentum and Si the spin angular momentum. The contribution of the latter "allows" singlet–triplet transition in absorption or emission CD.[3] A similar situation is encountered in magnetic circular dichroism (MCD), where the inclusion of the spin angular momentum in the magnetic dipole operator enables the observation of singlet–triplet transitions in short optical cells.[5,6]

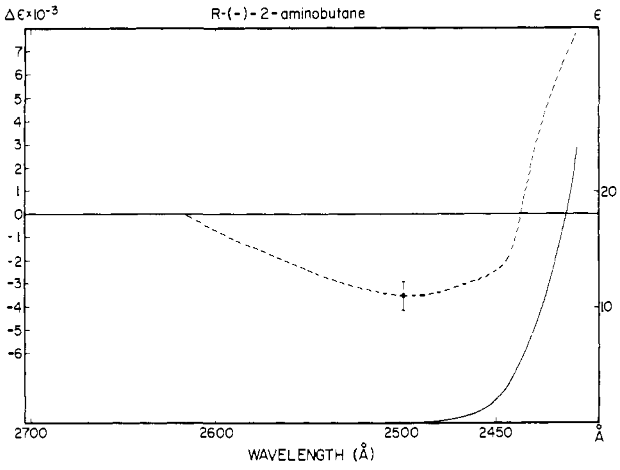


Figure 1. The absorption and CD spectra of (R)-(−)-2-aminobutane in the gas phase. The spectral resolution for both spectra is 1.6 nm.

We report that, using the R-(−) and S-(+) enantiomers of 2-aminobutane (Nores Laboratories Inc.), we have indeed succeeded in detecting a CD signal at a lower energy than that of the first excited state and have assigned it as a singlet–triplet transition. This transition is observed in both solution and gas phases. The gas-phase measurements were carried out on a vacuum UV CD apparatus, which has been previously described.[7] The CD and absorption measurements were carried out over the wavelength region of 260–150 nm. The gas-phase measurements were carried out in an 11-cm optical cell using the equilibrium vapor pressure of the 2-aminobutane. The vapor pressure (75 Torr at 22 °C) was measured by using a Wallace and Tiernan absolute pressure gauge. The 2-aminobutane was used without further purification. The vacuum UV results will be reported elsewhere. The solution studies were performed on a Cary 60 instrument and were repeated on a JASCO J500 and found to be identical.

As an alkylamine, 2-aminobutane was expected to show absorptions characteristic for the amine chromophore. The spectra of ammonia and alkylamines are dominated by Rydberg transitions,[8] the lowest in energy being the n → 3s. This latter state is observed for 2-aminobutane at 212 nm in the gas phase and 206 nm in hexane solution. In perfluoro-*n*-hexane it is further shifted to the blue. This is typical behavior for a Rydberg state.[8] The CD sign for this state is positive for the R-(−) and negative for the S-(+) enantiomers. These CD signs were observed in the gas phase and hexane and C_6F_{14} solutions.

Considering, however, that circular dichroism is a modulation technique and, therefore, more sensitive than absorption measurements,[9] few cases have been reported where signals in CD were observed without corresponding absorption peaks.[10] We have observed a further example of this rare phenomenon upon extending our CD and absorption measurements to energies lower than the n → 3s. In Figure 1 we present the absorption and CD spectra of (R)-(−)-2-aminobutane in the gas phase. The figure reveals the tail of the n → 3s absorption band and the positive CD spectrum of this same transition. A different transition peaking at 215 nm and demonstrating an opposite sign in CD and

---

[1] McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice-Hall: Englewood Cliffs, NJ, 1969.

[2] Kuppermann, A.; Flicker, W. M.; Mosher, O. A. *Chem. Rev.* **1979**, *79*, 77.

[3] Steinberg, N.; Gafni, A.; Steinberg, I. Z. *J. Am. Chem. Soc.* **1981**, *103*, 1636.

[4] Schellman, J. A. *Chem. Rev.* **1975**, *75*, 323.

[5] Lindner, R. E.; Barth, G.; Bannenberg, E.; Djerassi, C.; Seamans, L.; Moscowits, A. *Chem. Phys. Lett.* **1976**, *39*, 411.

[6] Osborne, G. A. *J. Mol. Spectrosc.* **1974**, *49*, 48.

[7] Gedanken, A.; Levi, M. *Rev. Sci. Instrum.* **1971**, *48*, 1661.

[8] Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press Inc.: New York, 1974 (Vol. 1) and 1985 (Vol. 3).

[9] Stephens, P. J. *Annu. Rev. Phys. Chem.* **1974**, *25*, 201.

[10] Douglas, I. N.; Grinter, R.; Thomson, A. J. *Chem. Phys. Lett.* **1974**, *28*, 192.

0002-7863/89/1511-9237$01.50/0

very weak absorption (0 within our sensitivity) is observed. As expected, the *S*-(+) enantiomer yielded a mirror image reflected spectrum. The same sign CD band is observed in hexane and perfluoro-*n*-hexane solutions. This band obeys Beer-Lambert's rule, thus eliminating the possibility that hydrogen-bonded dimers are responsible for this band. This transition undergoes a small blue shift in solution where the peak is shifted from 251 nm in the gas phase to 246 nm in hexane solution. A similar blue shift, although somewhat larger, is obtained for the n → 3s Rydberg transition.

These observations lead us to believe that an excited state at an energy lower than the n → 3s is responsible for the observed signal. We believe this band to be the triplet component of the n → 3s Rydberg transition (whose singlet maximum is detected at 212 nm in the gas phase) for the following three reasons. Firstly, as we have already noted, this band precedes all the singlet states of the molecule. Secondly, the upper limit for the molar extinction coefficient of this transition is estimated as 0.2; singlet states, even forbidden, will have higher ϵ values through various borrowing mechanisms. Finally, the singlet-triplet energy splitting of 2-aminobutane is similar to that of ammonia and methylamine. The singlet-triplet splitting for the latter two compounds was determined[11] from the energy differences of the onset of the two transitions. It was found as 0.39 ± 0.1 eV for ammonia and 0.34 + 0.1 eV for methylamine. Taking the onset for the triplet at 262 nm and for the singlet at 247.5 nm yields a splitting of 0.28 eV for 2-aminobutane. The negative signal observed for this new state might also explain the negative optical rotation as expressed by the $[\alpha]_D$, since the $[\alpha]_D$ sign is associated with the CD sign of the first excited state. Whenever there is a mismatch between the sign of the $[\alpha]_D$ and the CD sign of the first excited state, higher excited states are then invoked to explain this mismatch. It is possible that in many cases triplets might be the explanation.

Acknowledgment. We thank D. Amar for helping with our measurements with the JASCO instrument.

---

[11] Abuain, T.; Walken, I. C.; Dance, D. F. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 641.

New Chiral Auxiliaries for Thermal Cycloadditions

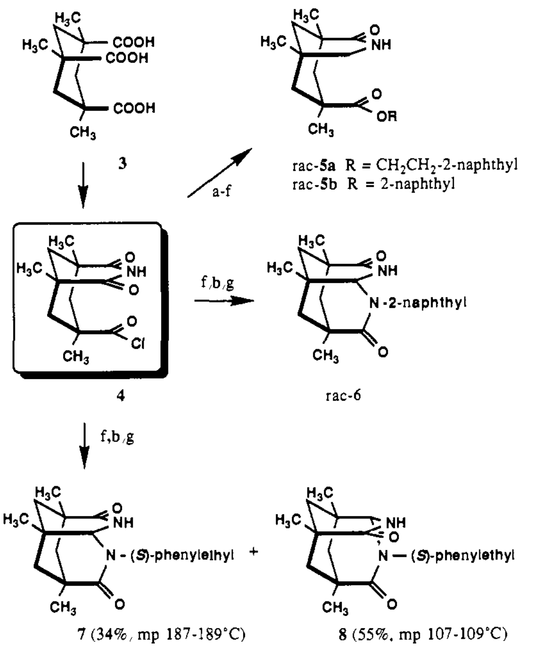
Dennis P. Curran,*[,1] Kyu-Sung Jeong,[2] Timothy A. Heffner, and Julius Rebek, Jr.*[,2]

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received July 6, 1989

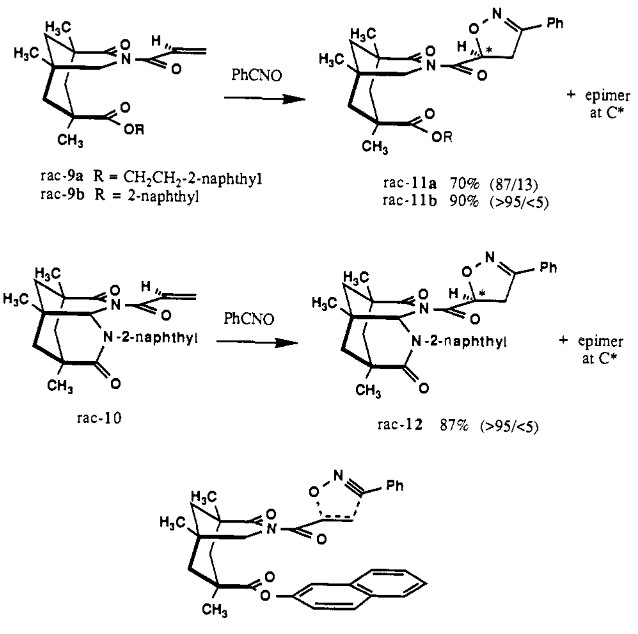
Although there are now several chiral acrylate derivatives that provide exceptionally high levels of asymmetric induction in Lewis acid promoted Diels-Alder reactions,[3] achieving these high levels of induction without the aid of a Lewis acid is often much more difficult. Because many important transformations are not subject to Lewis acid promotion, the development of new chiral auxiliaries that permit high levels of asymmetric induction in thermal addition and cycloaddition reactions of alkenes is an important goal.[3b,d]

Scheme I[a]



[a] Steps: (a) MeOH; (b) $NaBH_4$, EtOH; (c) Et_3SiH, TFA; (d) NaOH; (e) $SOCl_2$; (f) ROH or RNH_2; (g) pTsOH, CH_2Cl_2.

Scheme II



transition state model for 9b

Cycloaddition reactions of nitrile oxides provide a challenge for the development of new chiral auxiliaries (X_c) because the interaction between the incoming nitrile oxide and the auxiliary is at a bare minimum: the forming ring in the transition state[4] is roughly planar, and the two atoms nearest the auxiliary (O and N) bear no substituents while the most remote atom (C) bears a lone substituent that projects away from the chiral auxiliary (see Figure 1).[5] Any chiral auxiliary that exhibits high asymmetric induction in a nitrile oxide cycloaddition might be generally useful for other thermal addition and cycloaddition reactions as well. Among the many auxiliaries that have been surveyed,[6] only

---

[1] Dreyfus Teacher-Scholar, 1985-1989; Recipient of a National Institutes of Health Career Development Award, 1987-1992.

[2] Current address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

[3] Leading references: (a) Paquette, L. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, pp 456-478. (b) Helmchen, G.; Karge, R.; Weetman, J. In *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: Berlin, 1986; Vol. 4, pp 262-306. (c) Loncharich, R. J.; Schwartz, T. R.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 14. (d) Davies, S. G. *Chem. Br.* **1989**, *25*, 268. See also ref 6 and 8.

[4] Houk, K. N.; Duh, H.-Y.; Wu, Y.-D.; Moses, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 2754.

[5] Indeed, it is a characteristic of nitrile oxide cycloadditions to chiral acrylates that the degree of asymmetric induction does not depend on the nitrile oxide substituent. See ref 6 and 8.

[6] Recent examples and leading references: (a) Curran, D. P.; Kim, B. H.; Piyasena, H. P.; Loncharich, R. J.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 2137. (b) Olsson, T.; Stern, K.; Sundell, S. *J. Org. Chem.* **1988**, *53*, 2468.

0002-7863/89/1511-9238$01.50/0