Electron Density Distribution in the Olefinic Double Bond between Pyramidalized Carbon Atoms of a syn-Sesquinorbornene[1]

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Figure 1. Molecular structure of **1**.

Whereas experimental data concerning electron density distributions in bent C–C single bonds abound,[2] only very few C=C double bond systems deformed out of standard geometry have been investigated.[3] We have now determined by low-temperature (103 K) X-ray diffraction using the X–X method[4] the difference density in the central C=C double bond of the syn-sesquinorbornene syn-1′,2′,3′,4′,5′,6′,7′,8′-octahydro-6′-(phenylsulfonyl)spiro[cyclopropane-1,9′-[1,4:5,8]dimethanonaphthalene] (**1**) (Figure 1).[5] The carbon atoms of this double bond are strongly pyramidalized. An earlier crystal structure determination at room temperature established the bending at the double bond to be 17.2°.[6] The low-temperature value of 17.8° is similar (C3, C4, C5, C6/C10, C5, C4, C13 = 162.2°; Figure 1). When further comparison is made with the room-temperature data,[6] the bonds measured at 103 K are seen to exhibit longer distances, primarily as a result of the smaller thermal vibrations and the high-order refinement procedure.[5] The length of the double bond C4–C5 is 1.358 (2) Å (1.329 Å at room temperature).[6] The bond angles at the sp²-hybridized carbon atoms deviate substantially from standard values: 107.5 (1)°–108.4 (1)° for the endocyclic angles and 140.0 (1)°–140.2 (1)° for the exocyclic angles. The C3–C7–C6 bond angle of the spirocyclopropane is compressed to 96.7 (1)° within the polycyclic system. Consequently, the opposite cyclopropane angle C8–C7–C9 widens to 61.5 (1)°, causing lengthening of the distal C8–C9 bond to 1.526 (3) Å relative to C7–C8 (1.491 (2) Å) and C7–C9 (1.496 (2) Å). The electron-withdrawing property of the sulfonyl group and repulsive forces at O1···C9 (3.088 Å) promote pronounced lengthening of the C1–C6 bond (1.582 (2) Å), the longest bond in this molecule.

Difference density calculations were made in the molecular mirror plane of **1** (the phenylsulfonyl substituent excluded). This
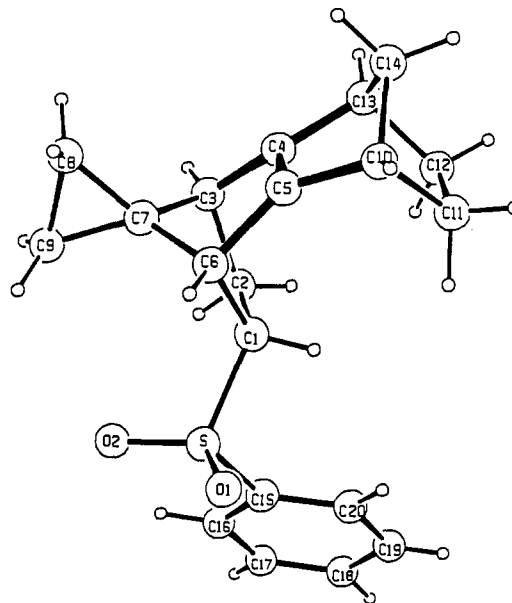
(1) Paper 8 in the series dealing with difference electron densities in strained polycyclic molecules. Part 7: Irngartinger, H.; Reimann, W.; Dowd, P.; Garner, P. *J. Chem. Soc., Chem. Commun.* Submitted for publication. Paper 50 in the series dealing with isodicyclopentadienes and related molecules. Part 49: Paquette, L. A.; Shen, C.-C. *J. Am. Chem. Soc.* In press.

(2) Coppens, P.; Hall, M. B. *Electron Distributions and the Chemical Bond*; Plenum Press: New York and London, 1982.

(3) Irngartinger, H.; Nixdorf, M. *Chem. Ber.* **1988**, *121*, 679.

(4) (a) Coppens, P. *Angew. Chem.* **1977**, *89*, 33; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 32. (b) Angermund, K.; Claus, K. H.; Goddard, R.; Krüger, C. *Angew. Chem.* **1985**, *97*, 241; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 237.

(5) Crystallographic data of **1** at 103 K: A suitable crystal with the dimensions 0.5 × 0.5 × 0.3 mm (from hexane) was selected. Cell dimensions were determined by a least-squares method from 97 high-order reflections: $a = 8.650$ (1) Å, $b = 10.315$ (1) Å, $c = 11.421$ (1) Å; $\alpha = 107.48$ (1)°, $\beta = 112.02$ (1)°, $\gamma = 106.37$ (1)°. The unit cell was chosen differently from that of the room-temperature structure determination;[6] triclinic space group $P\bar{1}$; $Z = 2$; $\mu_{calcd} = 1.34$ g/cm³. Two unique data sets with a total number of 19 896 intensities have been collected and averaged ($R_{int} = 0.029$) (Enraf-Nonius CAD4 diffractometer, Mo Kα radiation, graphite monochromator): $\sin \theta/\lambda = 0$–0.7 Å⁻¹, 3399 observed reflections ($I \geq 3\sigma(I)$) for calculation of the difference densities; $\sin \theta/\lambda = 0.7$–1.2 Å⁻¹, 4957 reflections (including 1468 unobserved reflections ($I \leq 3\sigma(I)$)) for the refinement with reflections of high order (C, O, S anisotropic, full matrix); $R = 0.039$. The positional and the isotropic thermal parameters of the H atoms have been determined within the low-order refinement ($\sin \theta/\lambda = 0.7$ Å⁻¹; $R = 0.034$). For the difference densities, the C–H bond distances are fixed at 1.08 Å. Corrections for absorption and anomalous dispersion but not for extinction have been applied.

(6) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. *J. Am. Chem. Soc.* **1983**, *105*, 3136.
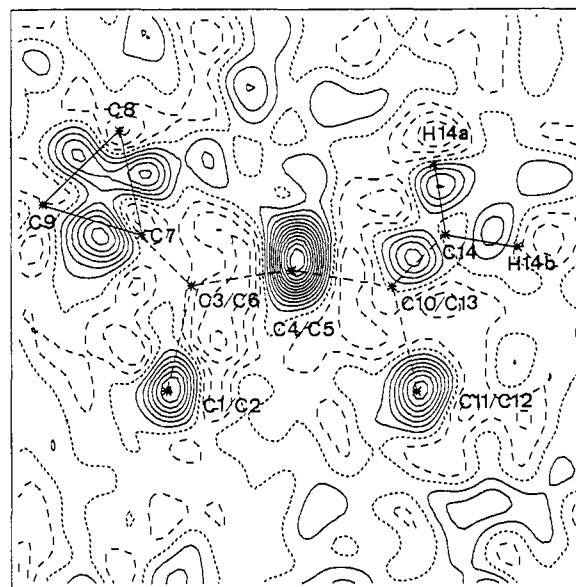
Figure 2. Deformation densities in a section through the centers of the bonds C1–C2, C4–C5, and C11–C12 perpendicular to these bonds. The contour intervals are 0.05 e Å⁻³. The zero line is dotted, and negative regions have dashed lines. The average standard deviation in the bonding regions is 0.05 e Å⁻³.

section cuts the C4–C5 double bond and the C1–C2 and C11–C12 single bonds perpendicularly at their midpoints and contains in addition the three-membered-ring plane C7, C8, C9 (Figure 2). The density maximum of the C4–C5 double bond, with its height of 0.67 e Å⁻³, is displaced only by 0.1 Å from the internuclear line into the exo direction. Particularly striking is the small shift parameter, despite the strong pyramidalization of atoms C4 and C5 and the corresponding structural deformation of the double-bond system. Obviously, it is more difficult to accomplish deformation of a double bond than a single bond, as was shown earlier in the cyclobutadiene system.[3] The small experimentally determined shift is in agreement with the calculations of Gleiter et al.[7] and Houk et al.,[8] who, contrary to Fukui et al.,[9] estimated only small sp mixing in the HOMOs of norbornene and syn-

(7) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron Lett.* **1982**, *23*, 2435.

(8) Houk, K. N.; Rondan, N. G.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmeyer, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 5980.

(9) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054.

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°).

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

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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,

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

where Li is the orbital angular momentum and Si the spin angular

(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.

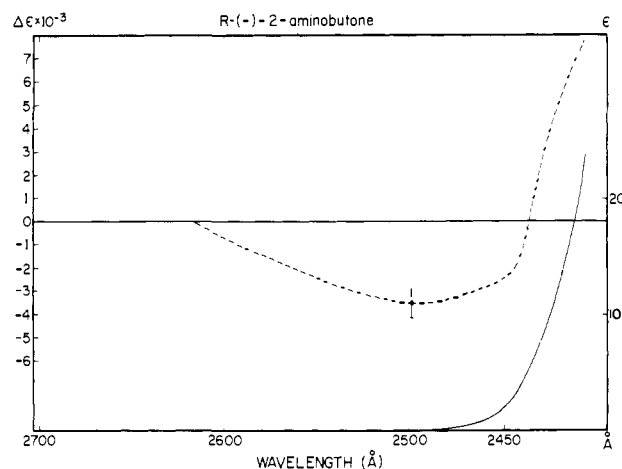(4) Schellman, J. A. *Chem. Rev.* **1975**, *75*, 323.

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.

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]

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 $\rightarrow$ 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 $\rightarrow$ 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 $\rightarrow$ 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

(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.